ISSN 0704-3716

Canadian Translation of Fisheries and Aquatic Sciences

No. 5396

Criteria for the definition of salinity of sea water by electroconductivity with correction for temperature and pressure

P. N. Yerofeyev, L. G. Ponomareva, and A. N. Ramazin

Original title: Unknown

In: Series 9, Release 4, 1975. Moscow

Published by: Central Scientific Research Institute of Information and Technico-Economic Research, Ministry of Fisheries of USSR

Original language: Russian

Available from:
Canada Institute for Scientific and Technical Information
National Research Council
Ottawa, Ontario, Canada K1A 0S2

1988

56 typescript pages

ABSTRACT

This summary compares salinity equations with methods and definitions; investigates uncertainties of sea water composition, effects of temperature, depth and biochemical processes on electroconductivity of sea water; and delineates relationships between electroconductivity and salinity. Theoretical and empirical formulas describing this relationship are outlined, as are effects of temperature and depth on electroconductivity measured in situ and subsequently used to calculate salinity. Questions of proper static and dynamic calibration of laboratory and in situ salinometers are also discussed.

INTRODUCTION

The contemporary stage of development of oceanology is characterized by a transition to new methods with increasing automation. At the present time, expeditionary oceanographic work is strongly dependent upon automated instruments and systems for determining water temperature, specific electrical conductivity, salinity and hydrostatic pressure (measured depths). With this apparatus, data are derived about spatial variability in hydrological characteristics of sea waters. Salinity is usually calculated from specific electrical conductivity, temperature, and hydrostatic pressure. In some instruments a series of circuits compensates for temperature and hydrostatic pressure and the instruments give results in terms of salinity.

The advent of automated apparatus has posed a series of problems:

(a) How to evaluate the error of measurement of salinity;
(b) What counts as an instrument error, and what is physically real is not always evident;
(c) How to calibrate apparatus in laboratories and under ocean conditions and what to accept by way of supporting standard values;
(d) What are the existing methods of calculating salinity from specific electrical conductivity.

The biggest difficulties appear in evaluating the instrument calibrations since here are focused the effects of all assumptions and inaccuracies accepted in standard values and methods of calculation. For example, in calibration at sea, in situ instruments are compared with water samples brought to the surface in oceanographic bottles. When the bottles are lifted to the surface, temperature and pressure changes occur which destroy the established equilibrium and change the chemical composition. In the process, as R. Horne (19) has pointed out, not only the forms in which particles can be found change, but if the sample during the rise in temperature and lowering of pressure loses gases dissolved in it, then this may change the general contents for some of the chemical elements.

The influence of similar phenomena on the results of measurement, in practice does not lend itself to correction by calculation.

This example illustrates the complexity of the problems of the definition of salinity not only in automated devices, but also in chemical analysis. It is not by chance that, up until now, scientists' attention has been occupied by the problem of "salinity". Out of the development of very good measurement of characteristics came an information flow.

After the first edition of the International Oceanological Tables and results, a comparatively small number of papers (27, 48, 70, 106, 113) addressed the applicability of the formulae of Knudsen to chemically altered waters, the form of the formulae connecting S-Cl for these waters and the improvement of volumetric methods of determining salinity. In the late '50's and the first half of the 60's many articles appeared noting the electrochemical methods, basically conductometric, of determining salinity and also addressing the question of salinity-chlorinity/electroconductivity of ocean

waters (10, 38, 62, 53, 93). Here it is especially necessary to note the basic work of the UNESCO groups (37, 39, 40, 41, 115, 116, 117) the results being the base of the new International Oceanographic Tables (9). Works coming out at the same time, investigated waters from various regions of the world's ocean with modified saline constitutions (12, 15, 74, 78, 82, 86).

The superior instrumental resolution of conductometric methods exposed the variability in the macrocomposition of waters of the open ocean and led to reports on such topics as the determination of ions in the macrocomposition and variations of their chlorine ratios, the physiochemical states and the degree of disassociation of these ions depending on surrounding conditions (temperature, pressure, pH, etc.) partial electroconductivity of ions, coefficients of activity, influence on electrical conductivity of biochemical processes and finally investigation of theoretical questions of thermodynamics and electrochemistry of seawater. From 1966-1970, at least 300 works appeared in these fields. The fundamental questions and summary of existing knowledge of these problems are contained in a recently published monograph (in Russian) by R. Horne, "Chemistry of the Sea" (19).

The increasing use of highly sensitive sensors in in situ instruments has forced the researchers to consider the questions of the realistic accuracies attainable by such instruments in actual oceanic conditions. The results of this are a growing collection of articles on ocean design - specification data on salinity measurements and interpretations together with a noticeable decline in the number of works on the construction of instruments.

In spite of this abundance of information there is an absence of summary review works, correlating individual aspects of the problems of "salinity", starting from the actual understanding of "salinity", and ending with an appraisal of results of recent changes. This work is an attempt to fill this gap.

THE CONCEPT OF SALINITY

The most general, and at the same time, the most exact definition of salinity may be considered the weight of all materials dissolved in a unit volume (or a weight) of sea water. However, attempts to define this weight have met with many difficulties, and have resulted in a whole series of stipulations connected with the weight analysis of samples of water for salinity. A simple evaporation of the sample is accompanied by salt losses, caused by heating the volatile compounds; the hydroscopic property of the thick residue impedes the measurement of its stable constant weight. To overcome the difficulties of analysis, Forch, Knudsen and Sorensen proposed their method to define a dry residue; the sample of seawater is processed with hydrochloric acid then, in an aqueous solution of chlorine, is evaporated and dried to a stable weight at 480°C. To the resulting weight of the dry residue are introduced corrections for the loss of chlorine at evaporation and loss of weight in the air. By this method, the authors (48) defined salinity as "the weight of dissolved solids brought to a vacuum, derived from one kg. of seawater with all halogens replaced by equivalent quantities of chlorine, carbonates converted to oxides and organic matter burned out".

This formula was later refined by stipulating that during the processing of the sample in hydrochloric acid the carbonates are transformed to chlorides; and not into oxides (21). The amended formulation defines salinity as the "quantity of solid dissolved materials, contained in 1 kg. of seawater with the condition that halogens and carbonates are mixed with equivalent quantities of chlorine, and the organic matter burned off".

In this manner, definitions of salinity are developed which though closer to the true value, are still conditional and related to the methods of analysis.

Because of the great technical difficulties of weight analysis of salinity and the impossibility of adapting it to marine conditions, it was essential to define another method. Based on the premise of stable consistency of sea water and taking into account the technical advantage of volumetric definition of chlorine content, Knudsen tied together salinity (nine samples) arrived at by weighing, with the halogen content (chlorinity) and derived the relation:

$$S°/_{oo} = 0.030 + 1.8050\ Cl°/_{oo} \qquad [1]$$

Chlorinity, in its turn, is represented as "the weight in grams of silver (atomic weight) essential for the exact precipitation of halogens in 0.3285234 kg of given seawater" (4). In addition, formula [1] is based on the condition about constant content of sea water, although Knudsen had already considered that discrepancies in parallel definitions of "weight salinity" caused by the variation of salt content could reach .012°/$_{oo}$.

Later it was established (2, 23, 67) that Knudsen's formula was a particular case of the formula of mixing

$$S°/_{oo} = a + bCl°/_{oo} \qquad [2]$$

where the value "a" is dependent on the saline composition of the waters of continental runoff diluted with ocean water (Table 1). In a lesser degree the contents of continental runoff waters also influence the value of the coefficient "b". Selecting the coefficients as applicable to certain regions of the world's ocean, subjected to the influence of continental runoff, "we bring the local influence into the salinity-chlorinity equations". (23).

TABLE 1

Values of coefficient "a" for metamorphasized waters from A.P. Tsurikova and V.L. Tsurikov (23)

Values of coefficient a°/$_{oo}$	Authors	Regions
0.1856	Nikiten, Kondratev, Yuriev 1955	Black Sea
0.230	Tsurikova 1960	Azov Sea
0.115	Zarinsh, Ozolinsh 1935	Baltic Sea
0.250	Yuryavichus 1961	Baltic Sea
0.03	Knudsen 1902	Baltic Sea

Excluding the local characters of coefficients, the relationship between salinity and chlorinity has the form:

$$S°/_{oo} = bCl°/_{oo} \qquad [3]$$

This equation is interpreted in the sense that for any sample of water the relationship between salinity and chlorinity is constant, and the withdrawal or addition of fresh water will not exert an influence on coefficient "b". To a first approximation for the waters of the open ocean it may be postulated that water exchange follows the path of evaporation and precipitation, that is, oceanic water mixes practically with non-mineralized water (47). Strictly speaking, the coefficient "b" for various regions of the ocean is different, and its value is determined by two considerations: (a) coefficient "b" must correspond to the average ratio of salinity to chlorinity; (b) salinity defined by equation [3] must agree with earlier definitions. Guided by these considerations, the united group working with the equations of sea water derived the equation [1], (8, 47):

$$bCl°/_{oo} = 0.03 + 1.8050Cl°/_{oo} = 35°/_{oo}$$

For a mean chlorine content of 55.35% coefficient "b" has the value of 1.80655 and equation [3] becomes:

$$S°/_{oo} = 1.80655Cl°/_{oo} \qquad [3^1]$$

The differences between values of salinity calculated with equations [1] and [3^1] are given by formula

$$\Delta S = S_1 - S_2 = 0.03 + 1.8050Cl - 1.80655Cl$$

where S_1 - salinity by formula [1] and S_2 - salinity by formula [3^1].

For the range of salinity 0 to $40°/_{oo}$ the discrepancies are as follows:

$S°/_{oo}$	$\Delta S°/_{oo}$
0	0.03
10	0.021
20	0.013
30	0.004
35	0.000
40	-0.004

Discrepancies for open ocean ranges of salinity are not great and thus formula [3^1] is recommended as a new definition for salinity (124).

Apart from above formulations which are usually cited in practice, Lyman and Fleming (77) proposed understanding by the term the sum of ions: $\Sigma°/_{oo}$ - the total mass of major ions dissolved in one kg. of seawater macrocomposition (chlorine, bromine, fluorine, sulphate, nitrate, potassium, magnesium, strontium) and undissociated boracic acid. The $\Sigma°/_{oo}$ is linked with $Cl°/_{oo}$ by the relationship:

$$\Sigma^{\circ}/_{\circ\circ} = 0.073 + 1.8110 Cl^{\circ}/_{\circ\circ} \quad [4]$$

or, by analogy with formula [3] by

$$\Sigma^{\circ}/_{\circ\circ} = 1.8148 Cl^{\circ}/_{\circ\circ} \quad [5]$$

To go from salinity to the sum of ions, C.V. Bruyevich obtained the value of corrections on the translation of carbonates into oxide (with the expression of carbonates in the form of ion CO_3^{-2}) and the translation of bromine into chlorine (4) as:

$$\Sigma^{\circ}/_{\circ\circ} - S^{\circ}/_{\circ\circ} = 0.088^{\circ}/_{\circ\circ}$$

In the work (23) are the relationships of salinities calculated by formulae [1] and [3¹] with the sum of the ions by [4] and [5]:

$$\Sigma^{\circ}/_{\circ\circ} = 0.043 + 1.0033 S^{\circ}/_{\circ\circ} \quad [6]$$

$$\Sigma^{\circ}/_{\circ\circ} = 1.0045 S^{\circ}/_{\circ\circ} \quad [7]$$

Inasmuch as the sum of the ions includes only nine components of the saline content of sea water, it underestimates true salinity. The relationships [6] and [7] indicate the excess of $\Sigma^{\circ}/_{\circ\circ}$ over salinity in the accepted definitions. The value of this excess grows with the increase of salinity from $0.043^{\circ}/_{\circ\circ}$ with $S = 0^{\circ}/_{\circ\circ}$ and to $0.116^{\circ}/_{\circ\circ}$ with $S = 35^{\circ}/_{\circ\circ}$ if one uses formula [6] and from $0.000^{\circ}/_{\circ\circ}$ to $0.116^{\circ}/_{\circ\circ}$ with those salinities calculated by formula [7] (23). Consequently salinity, defined by these interrelationships, is to a large extent underestimated with regard to true salinity.

As regards to metamorphasized waters, that is, waters of coastal regions of the ocean, partly isolated seas, or peculiar regions of the world's oceans, such for example, as regions of intensive carbonate precipitation (Bahama Banks) (29, 110) or deep "brine" of the Red Sea (33), none of the cited formulae is applicable. The opinion of the authors of article (23) regarding the necessity of special interrelationships for metamorphasized waters is indisputable.

All the above cited relationships are based on chemical analysis definitions of the separate components of the saline content (chlorinity, major ions) empirically connected with the values of the dry residue of Forch et al. The growth in popularity of the conductivity method of determining salinity has necessitated a clarification of the relation of the mineralization of sea water with its electrical conductivity. It is significant that such works have been undertaken by several investigators (12, 15, 25, 27, 30, 85, 103, 106, 113). However, the results of each of these investigators is limited either by the locality of the sample taken or by the errors of the conductometers or their definitions of chlorinity and salinity. In connection with this, a work group has already carried out a program from the results of which there were derived formulae connecting electrical conductivity with salinity, chlorinity, and the density of sea water. The fundamental part of the work was undertaken in Great Britain under Dr. Roland Cox. From a thorough analysis of the water samples, taken from the top 100 metre layer of the world ocean and also from the Baltic, Black, the Mediterranean and Red

Seas (a map of the sample locations is shown in (41)), a relationship was demonstrated linking salinity with relative electrical conductivity at 15°C and pressure of 1 atmosphere:

$$S^{\circ}/_{\circ\circ} = -0.08996 + 28.29720R_{15} + 12.80832R_{15}^2 - \quad [8]$$
$$10.67869R_{15}^3 + 5.98624R_{15}^4 - 1.32311R_{15}^5$$

Equation [8] served as the basis for the new International Oceanographical Tables (9) and was recommended by the working group ICES/SCOR/IAPSO/UNESCO and a "new definition of salinity" (124).

The principal advantage of linking electrical conductivity and salinity before linking chlorinity and salinity is that the first link is direct, defining the nature of sea water - electrolyte, the second empirical link, (chlorinity - salinity) is less exact than the first. But this practical advantage is entirely lost if it be remembered that the supporting values of salinity were calculated by chlorinity and formula [3¹] in its turn, is based on the weight definitions of salinity. Because of this it is hard to object to authors (23), who say that "formulae [8] and [3¹] are not 'new definitions' of salinity but are only other expressions of it".

We examined the understanding of "salinity", which in oceanographic literature was used for designating the quantity of solid matter dissolved; the quantity of dry residue according to Sorensen; the features defining equation [1]; the features defining equation [3¹], the features defining equation [8] the sums of ions $\Sigma^{\circ}/_{\circ\circ}$. The above expressions of the understanding of "salinity" correspond only under conditions where the relations of salt ions are constant. The discrepancies between the various calculations of salinity were greater, the higher the variation of values of concentration of ions in the macrocontents.

THE PROBLEM OF "CONSTANCY OF THE CONTENTS" OF SEA WATER

A. Marcet made the first statements of the constancy of sea water based on analyses of water from the Arctic and Antarctic Oceans, and the Mediterranean, Black, Baltic, Yellow, East and South China Seas and the White Sea. These are found in the first monograph on oceanography, by M. Maury "Physical Geography of the Sea" (19, 122) published in 1855. But Marcet's statement is not categorical but with the stipulation "like a law". Analysis of a sample from the "Challenger" cruise by Dittmar confirmed the constancy of the relation, but only in the second decimal in the equivalent salinity (46) (Table 2) and Marcet's principle was corroborated with the stipulation of "approximately" or "almost".

In this way, Dittmar demonstrated spatial changes in contents of sea water, which could not be accounted for by calculation of analysis errors. However, the concept of constancy of composition proved to be very useful, and thanks to that a new base was laid for a practical definition of salinity.

TABLE 2

Percent Contents of Macrocomponents of Sea Water - Dittmar's definition (3)

	Concentration %					
	Cl	SO_3	CaO	MgO	K_2O	Na_2O
Maximum	55.628	6.457	1.852	6.302	1.425	41.638
Minimum	55.190	6.321	1.585	6.115	1.273	41.215
Average	55.420	6.415	1.692	6.214	1.383	41.433
Difference between range	0.538	0.154	0.240	0.187	0.152	0.423
Difference % from average	0.97	2.4	14.2	3.00	11.4	1.00

TABLE 3

Ions	Concentration %			Atlantic-Indian	Atlantic Pacific	$\frac{\text{Atl-Ind}}{\text{Ind}} \times 100\%$	$\frac{\text{Atl-Pac}}{\text{Pac}} \times 100\%$
	Atlantic Ocean	Indian Ocean	Pacific Ocean				
From Calle (1943)							
Cl^-	55.09	55.44	55.29	-0.35	-0.20	- 0.63	- 0.36
Br^-	0.18	0.13	0.19	+0.05	-0.01	+ 38.50	- 5.27
SO_4^{-2}	7.89	7.79	7.72	+0.10	+0.17	+ 1.28	+ 2.20
CO_3^{-2}	0.20	0.05	0.25	+0.15	-0.05	+300.00	-20.00
Na^+	30.46	30.91	30.57	-0.45	-0.11	- 1.45	- 0.31
K^+	1.13	0.85	1.07	+0.32	+0.06	+ 37.70	+ 5.61
Ca^{+2}	1.26	1.16	1.19	+0.10	+0.07	+ 8.62	+ 5.88
Mg^{+2}	3.79	3.67	3.72	+0.12	+0.07	+ 3.27	+ 1.88
	100.00	100.00	100.00	Σ+0.04	+0.00		
# of samples	27	2					
From Nosikov, Okune, Maeda, Ogata (1939) and Calle (1943)							
Cl^-	55.30	55.38	55.53	-0.08	-0.23	- 0.14	- 0.41
SO_4^{-2}	7.91	7.91	7.67	0.00	+0.24	0.00	+ 3.14
Na^+	30.59	30.65	30.84	-0.06	-0.25	- 0.16	- 0.81
K^+	1.14	1.01	1.01	+0.13	+0.13	+ 12.86	+12.86
Ca^{+2}	1.26	1.25	1.22	+0.01	+0.25	+ 0.80	+20.66
Mg^{+2}	3.81	3.80	3.73	+0.01	+0.08	+ 0.26	+ 2.43
Σ	100.00	100.00	100.00	Σ+0.01	Σ+0.22		
# of Samples	>27	32	104				

At the same time variations in the content of ions of the macrocontent were recognized from the results of oceanographic indicators of water masses, river runoff, fractionalization at ice melting and ice formation, and also by ion exchange with the sea bottoms and suspension load. (1, 3, 20, 22, 31, 64, 76, 81, 84, 105, 107, 109, 114).

Obtaining these comparatively few data of the old definitions of the components of macrocontent, carried out with the aim of indication of the water masses or geochemical processes, required from the researchers a colossal expenditure of effort and time (in their time, there was no modern spectrophotometric and atom-absorption apparatus). At the present time modern instruments provide new illumination and essential information in attempts to interpret salinity data. In particular, L.K. Blinov's summary may be noted on the contents of the waters of the Atlantic, Pacific and Indian Oceans, resulting from the work of Calle, Nosikov, Okuno, Maeda, Ogata (Table 3). The contents of Table 3 provide evidence of discernable differences of the macrocontent of the ocean waters and of global geochemical results of fresh water runoff into the ocean, exchanging not only (and not so much) general salt content, but also the content of characteristic sea ions Cl^- and Na^+. Thus, in the Atlantic Ocean the content of these ions is somewhat lower by comparison with the Indian and especially with the Pacific Oceans, and the concentration of sulfate, magnesium and calcium is higher.

O.A. Alekin, analysing the significance of river ion runoff into the ocean, noted characteristic layers of unevenly distributed calcium to chlorine ratio. To an even greater degree the chemical composition of continental runoff has an influence on the basic saline content of those coastal waters whose exchange with open sea water is hindered. The graph (Figure 1) drawn by A.P. Purikov (21), for the waters of the Azov Sea, may serve as a general illustration of the variability of the saline content of diluted waters. A large number of works have been devoted to learning the contents of chemically different waters and the question connected with the applicability to conductive methods of definition of the mineralization of these waters requires a special examination. A summary of results of the basic saline content of the Baltic Sea is found in (11, 24, 74, 86). Morris and Riley (84) show noticeable differences in the composition of the fundamental ions of the Azov, Black and Baltic Seas; articles (78, 79, 82) are devoted to learning the basic saline and chlorine coefficient of ions of the Mediterranean Sea. Apart from continental runoff, the process of ion fractionation at the formation of ice and at its melting noted that there exist a large number of reliable work, indicating similarity in the saline content of sea water, but there is an even greater number of just as reliable data, giving evidence to the contrary. At the present time the fact of nonsimilarity of ion contents of sea ice, and water is shown in (20, 22). However the influence of the processes of ice formation and melting on the changes of electrical conductivity because of changes of saline content is not up to now accepted (22, 23, 47).

The influences on the content of basic ions through the process of ion exchange with suspension and sea bottom is given in (81).

In addition, in the determinations of average saline content of sea water, biogeochemical processes take part. Lyman (76) determined that extreme variations in content of biogenic elements and alkalinities have an

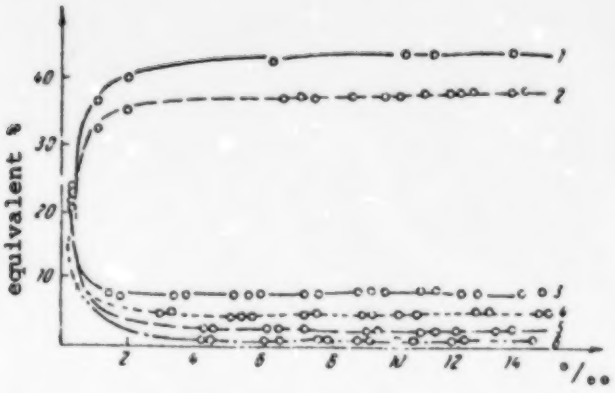


Figure 1. The dependence between general salinity and the ion content of waters of Azov Sea according to (21).

effect on the limit of error of definition of salinity by chlorinity of (0.02 °/₀₀). Particularly biogeochemical processes have an effect on vertical distribution of calcium and other components of the carbonate system. Quantitative data about chlorine coefficients and calcium contents are given in (29, 64, 105, 107, 110, 114).

Summaries of contemporary knowledge about chlorine ratios of the main components of sea water are given in Tables 4 (33) and 5 (19).

TABLE 4

Component	Chlorine Coefficient (g/kg/Cl °/₀₀)				# of Samples	Literature Sources
	Average Value	Standard Deviation	Maximum Value	Minimum Value		
Na	0.5555	0.0007	0.5572	0.5535	49	44
	0.5567	0.0007	0.5576	0.5555	93	105
Mg	0.06692	0.00004	0.06713	0.06669	66	44
	0.06667	0.00007	0.06689	0.06641	91	105
SO_4	0.1400	0.0002	0.1406	0.1394	345	84
Ca	0.02126	0.00004	0.02134	0.02115	66	44
	0.02128	0.00006	0.02150	0.02110	81	105
K	0.0206	0.002	0.0209	0.0203	54	44
	0.0206	0.002	0.0209	0.0203	84	105
HCO_3	0.00749	0.00008	0.00791	0.00707	-	71,101,90
Br	0.0003473	0.000012	0.003509	0.003439	211	84
B	0.00240	0.000005	0.000264	0.000222	-	43
Sr	0.00040	0.00002	0.00041	0.00038	58	44
	0.00042	0.00002	0.00044	0.00040	38	105
F	0.000067	0.000001	0.000090	0.000064	300	52,104

Total variation of saline content of sea water of the open ocean in the opinion of Carrit and Carpenter (31), may cause an error of accepted relationship Cℓ-S of 0.04 °/₀₀ (of salinity); Cox (38) gives a value of 0.06 °/₀₀.

THE INFLUENCE OF CHANGES IN THE BASIC SALINE CONTENT OF OCEAN WATERS ON THE RESULTS OF CONDUCTOMETRIC DEFINITIONS OF SALINITY

At the present time the variability of saline content of ocean waters is particularly important for evaluation of errors of definition of salinity (and also of chlorinity and density) by measurement of electrical conductivity.

To interconnect salinity and electrical conductivity the basic equation [3[1]] is used relating chlorinity and salinity of sea waters. This relation is based on the assumption that for all regions of the world's ocean the content of chlorine equals 100%/1.80655 = 55.35%. However, the percentage content of halogens (chlorinity) varies in some regions (Table 6) (3).

From the data of Table 6, the variations of chlorine content can reach values of 0.26% by Calle, 0.18% by Nasikava and Calle and 0.28% by Dittmar which for ranges of salinity 33 to 37 °/₀₀ can lead to errors in salinity equal correspondingly to 0.096; 0.067; and 0.104 °/₀₀. Cox's work (41, 117) shows that for two water samples with the same electrical conductivity, salinity defined by chlorinity, can have a discrepancy of 0.03 °/₀₀.

Error, related to the inconstancy of water composition can at first be approximated by differences between chlorinity values from electrical conductivity and chlorinity values defined by titration: $\Delta Cl = Cl_{el} - Cl_{tit}$. In the opinion of Sugiura (111), the value of the difference can serve as an indicator of the origin of water masses, its transformation under the activity of river runoff, or biogeochemical processes. More exactly, the value ΔCl defines the difference of saline composition of any water from the composition of the nine Knudsen samples. In the top 500 metre layer the value of ΔCl is usually negative; deeper than 1000 m it's positive (reasons for this will come later). Analysing this regularity, Sugiura considered not only the change of sign of ΔCl but also the necessity of calculating the total value "of parameter of saline composition", of standard water which is used for the calibration of salinometers inasmuch as such standards are usually prepared from the top layer of the ocean.

Attempts at explaining the effects of variability of concentration of the basic ions on electrical conductivity may be in general divided into two categories; "direct" experiments and "indirect" calculations. The first are founded on modelling of sea waters, experiments on models and applying conclusions and formulae of theoretical thermodynamics and electro-chemistry to the electrochemical system "sea water". Thus, in one of many works of this type (49) calculations are made regarding the quantity of the most important ions and their activities. Articles (68 and 102) are devoted to studying the effects of pressure and gravity on the solubility, degree of dissociation and activity of macrocomponents. Article (58) develops from the theory of electrical conductivity of electrolytes using data of experiments on sea water.

TABLE 5

Ref.#	Na	Mg	K	Ca	Sr	SO_4	Br
1.	-	-	0.02026	-	-	-	0.00337-0.00341
2.	0.5544-0.5547	0.0667	0.01953-0.0263	0.02122-0.2126	0.000420	0.01393	0.00325-0.0038
3.	0.5553	0.06632-0.06695	0.02096	0.02154	-	0.1396-0.1397	0.00348
4.	0.5497-0.5561	0.06627-0.0676	0.02125	0.02058-0.02128	0.000413-0.000420	0.1399	0.0033
5.	-	-	-	0.02099	0.000445	0.1399	0.0038
6.	0.5310-0.5528	0.06785	0.02008	-	-	0.1396	0.0034-0.0038
7.	0.5536	0.06693	-	0.02156	-	0.1414	0.00316-0.00344
8.	0.55184	-	0.0210	-	-	-	-
9.	0.5573	-	-	-	-	0.1397	0.0033
10.	0.5495-0.5562	-	0.0191	-	-	-	-
11.	0.5484	-	0.0211	-	-	-	-
12.	-	-	-	0.02120	0.000467	-	0.00347
13.	-	0.0676	-	0.02130	-	0.1394	-
14.	-	0.06742	-	0.02085	-	-	-
15.	-	-	-	-	0.000424	-	-
16.	-	-	-	-	-	0.1395	0.0043
17.	-	-	-	-	-	-	0.00327-0.00347
18.	-	-	-	-	-	-	0.00341
19.	-	-	-	-	-	-	0.00341

1. Central Atlantic
2. Atlantic Ocean
3. North Pacific
4. West Pacific
5. Indian Ocean
6. Mediterranean Sea
7. Baltic Sea
8. Black Sea
9. Irish Sea
10. Puget Sound
11. East Siberian Sea
12. Antarctic
13. Gulf of Tokyo
14. Barents Sea
15. Arctic Ocean
16. Red Sea
17. Japanese Sea
18. Bering Sea
19. Adriatic Sea

TABLE 6

Parameters	Variation of percent content of Cℓ and deviations from average (55.35‰)			
	Source	Atlantic Ocean	Indian Ocean	Pacific Ocean
Cℓ ΔCℓ ΔS	by Calle	55.09 0.26 0.096	55.44 -0.09 -0.033	55.29 0.06 0.02
Cℓ ΔCℓ ΔS	by Calle & Nasikava	55.30 0.05 0.019	55.38 -0.03 -0.01	55.53 -0.18 -0.067
		Maximum	Minimum	
Cℓ ΔCℓ ΔS	by Dittmar	55.628 0.28 0.104	55.190 0.16 0.06	

A series of works devoted to experimental definition of the coefficients of the activity of the separate ions in different conditions and the application of the resulting values for calculation of total electrical conductivity or corrections for changes of its values are found in (57, 65, 66, 97, 98, 99).

Some scientists have put their energies on the changes of the partial electrical conductivity of sea water and the subsequent calculation of total electroconductivities (34, 35, 88). All these articles provide only an incomplete picture in this direction. A fuller summary of contemporary status of the theory of electroconductivity of sea water is that by Horne (19).

From the scientists working in the "theoretical" field have come some interesting results but practically the use of these results provides as yet very inexact values. For example, formulae and experimental data of Conners and Park (34), allow calculation of electroconductivity and its related salinity with an exactness of only 1 $^{o}/_{oo}$. The development in this direction is held back by the lack of development of the theory of electroconductivity connected with the electrolyte, the extraordinary complexity of electroconductivity systems of "sea water", and the difficulty of modelling real conditions and conductance changes in situ.

The indirect approach is given in the works (51, 72) in which are defined the corrections on the change to salinity calculated from the International Tables. Such works usually repeat or reiterate that for some chlorinities, the relationships of Cox either are applicable or are non-applicable with stipulations and give conclusions of a regional character. However the authors of the work forming the basis for the International Tables did not claim a full correspondence of these to all the ranges of salinity of

all the regions of the world's oceans. Discussions following the publishing of the tables concluded with the recommendation of special tables for changed waters (23).

The papers (33) and (111) serve as examples of methods of evaluating the effects of changes of saline composition on the results of conductometric definitions of salinities. These works relate factual data of the contents of the macrocomponents to experimental values of partial electroconductivity and provide formulae, describing electroconductivity of sea water.

In reference (33) data are used about the variability of salt content (Table 5). Calculations of the gram molecular concentration of ions and the fluctuations of their compositions are used to establish the essential equivalent additions of "hypothetical" salts (Table 7). The calculations are carried out for the aforementioned anomalies of salt composition with negative anomalies accepted as equal to positive.

TABLE 7

Salt	Anomaly on 1 kg of sea water (S=35‰; Cℓ=19.375°/$_{oo}$) Mol/kg
$Ca(HCO_3)_2$	0.00007
MgF_2	0.00001
$MgSO_4$	0.00008

The Maximum Anomalies of Salt Content of Ocean Water, Expressed in Salt Form (33).

For the calculation of the total electroconductivity in (33) the authors used the values of partial electroconductivities from (35) and the formula:

$$K = \frac{\rho \Sigma_i c_i \lambda_i}{n(1 - x_s) + \rho \Sigma_i c_i V_i}$$

where K = specific electroconductivity; ρ = density of sea water; c_i = equivalent concentration of ions of type i; λ_i = partial equivalent electroconductivity of ion of type i; n = parameter, connected with temperature influence; x_s = mass of saline factors in sea water, V_i - partial volume of ions of type i. Calculations were carried out for temperature 25°C. For these values of total electroconductivity from the UNESCO tables, equivalent values of total salinities were found calculated from chlorinity by formula [3^1] (Table 8).

Of course, additions of "hypothetical" salts did not influence the value of chlorinity nor the value of salinity as a function of chlorinity. Electroconductivity fixed the addition to salinities of 0.008 °/$_{oo}$ for an actual addition of 0.014 °/$_{oo}$. From these calculations comes the result that the true salinity as estimated by chlorinity is accurate only to ±0.014 °/$_{oo}$, and by electroconductivity to ±0.006 °/$_{oo}$.

TABLE 8

Base Parameter	Anomalous calculated parameters	
	Cℓ°/₀₀	S°/₀₀
Chlorinity	0.000	0.000
Electroconductivity	0.004	0.008
Actual addition	0.000	0.014

The values of increase of parameters of water with additions of salts (refer to Table 7) in water salinity 35 °/₀₀ at T°=25°C (33)

The analogous calculations were carried out in (33) for coastal waters exposed to the influence of river runoff. An important peculiarity of this work was the choice of rivers and the definitions of types of chemical runoff in accordance with the classification of Gibbs (50). Thus for the Yukon River the runoff is characterized by a predominance of carbonates and bicarbonates over nitrates and chlorides; the Amazon River is typical of humid tropical regions with a prevalence of rain supplied rivers; the Rio Grande is a characteristic river of arid regions with waters of high mineralization and high average content of calcium and bicarbonates; for the Mississippi River the waters of which both by mineralization and by saline content are close to average of the world's river runoff. Applying analogous calculations of concentrations and anomalies, Conners and Kester calculated the composition of sea water with S = 35 °/₀₀ diluted with distilled water and river waters to salinities equal to 30 °/₀₀ (Table 9).

In the opinion of the authors (33) actual results require special examination, however the following values of errors in conductometric and titrometric methods of defining salinities for coastal waters (for extreme types of rivers) are considered to be quite well founded (Table 10).

Y. Sugiura (111), in investigating the different chlorinities and salinities defined by titration and conductometrically introduced a series of theoretical formulae taking into account all methods of analysis. The coefficients of his formulae (in a general view) took into account;

(a) losses by gravitational definitions,

(b) transformation of carbonates into oxide, etc.,

(c) the conditionality of the understanding of "chlorinity",

(d) the error of formula of calculating Cℓ in S,

(e) error of transformation from electroconductivity to S and Cℓ.

TABLE 9

Method of defining Salinity	Dilutors				
	Distillate	Amazon	Mississippi	Yukon	Rio Grande
$\Sigma°/_{oo}$	30.144	30.144	30.144	30.144	30.143
Weight	30.000	30.002	29.994	29.985	29.983
Elec. Conductivity	30.000	29.993	29.980	29.974	29.946
By Chlorinity	30.000	29.991	29.972	29.963	29.920

Salinity ($°/_{oo}$) of Sea Water, Obtained by Dilution of Waters Salinity ($35°/_{oo}$) with distilled and River Waters (33)

TABLE 10

Method	Error $°/_{oo}$	
	Amazon	Rio Grande
By chlorinity	0.009	0.08
By Elec. Cond.	0.007	0.054

On the basis of quantitative data (83) Sugiura calculated the differences of salinity defined gravimetrically and by titration, $\Delta G = S_{wei} - S_{titr}$, and conductiometrically and by titration $\Delta C = S_{el}-S_{titr}$, then compared the values ΔG and ΔC in pairs for the surface waters of the Baltic Sea and the open ocean, and the surface and subsurface waters of the ocean, the subsurface waters and the depths.

For the first comparison $\Delta G = S_{wei}-S_{titr}$ was considerably larger than $\Delta C = S_{el}-S_{titr}$. This, in the opinion of Sugiura, denotes the presence in Baltic water of an elevated (compared to the ocean) content of relatively inactive or heavy ions and ion complexes.

In the second comparison the value ΔG although close to the value ΔC in subsurface waters is evidently higher there than on the surface. One reason and evidently one of the more important reasons for this Sugiura counts as the increase in relative content of bicarbonates, in exchange for carbonates. This is stipulated in the increase of concentration of surface layers. Taking into account that 90% of carbonates but only 30% of bicarbonates exist as electrically neutral ion pairs, he concludes that movement from the left of the equilibrium $H_2CO_3 \rightleftarrows HCO_3^- \rightleftarrows CO_3^{-2}$ will give corresponding increases in electroconductivity.

In the third comparison the value ΔG for deep waters is higher than for subsurface waters, ΔC is lower. The increase of ΔG indicates, to a lesser degree, some lowering of the halogen content.

The decrease in electroconductivity of deeper water from calculation of change of constitution of waters was attributed to the dissolution of calcium carbonate and decreased concentration of free carbonic acid (by comparison with subsurface layers), which corresponds to a movement to the right in the above equilibrium relationship of the dissociation of carbonic acid and a lowering content of electroconductive ions.

Consideration leads one to conclude that for interpretation of in situ conductometric observations, calculation is necessary of geographic and temporal regularities of decreasing components of the carbonate system connected with the cycle of bioproduction.

Numerical data about the influence on electroconductivity elements of carbonate systems are found in (80, 87, 95). Park (87) found increased specific electroconductivity for dissolution of $CaCO_3$ of 6.10^{-3}mho/cm for 1 m mol dissolved carbonate; for exchange of 1 milli equivalent of carbonate with bicarbonate an increase of specific electroconductivity greater than 2.4×10^{-5} mho/cm (0.05%) (95). A shift of balance of carbonate systems is interrelated with decreasing pH. Variations in pH can cause errors in electroconductivity of 0.04%, equivalent to 0.012 $^{\circ}/_{\circ\circ}$ in salinity. It must therefore be taken into account in the derived figures which come from the author's reference (95) in laboratory experiments on waters, chlorinity $19^{\circ}/_{\circ\circ}$ at $T^{\circ} = 26^{\circ}C$ and atmospheric pressure. Authors (80) have evaluated the effects of systems of carbonic acid as 0.01 $^{\circ}/_{\circ\circ}$ in equivalent salinity.

Changes of electroconductivity corresponding to changes in equilibrium of systems of carbonic acid are illustrated in Figures 2 and 3 (95) andTable 11, derived from experiments of Grasshoff, (93).

TABLE 11

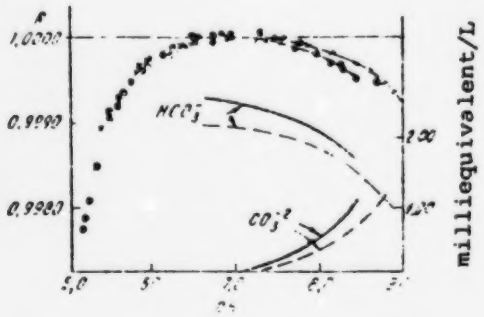
pH	Relative Electroconductivity	Corresponding Salinity	Salinity Deviation
8.4	1.00046	35.018	-0.012
8.3	1.00051	35.021	-0.009
8.2	1.00058	35.023	-0.007
8.1	1.00064	35.025	-0.005
8.0	1.00068	35.027	-0.003
7.9	1.00071	35.029	-0.001
7.8	1.00074	35.029	-0.001
7.7	1.00075	35.030	0.000
7.6	1.00076	35.030	0.000

NOTE: In all samples Chlorinity was constant

The balance of carbonic acid systems is connected with a spatial and temporal distribution of oxygen. Experiments to evaluate the effect of the concentration of oxygen on electroconductivity were carried out by Bradshaw (93). They showed that oceanic variations of content of oxygen, 0-7 ml/l, can cause deviations in electroconductivity corresponding to 0.003°/$_{\circ\circ}$ of salinity.

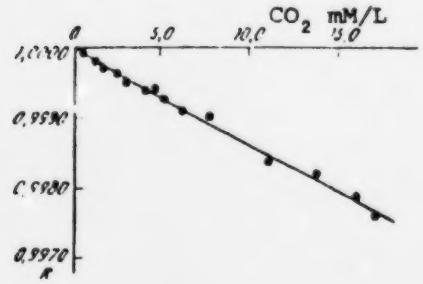
In the photic zone of variation of oxygen, biogenic matter, organics and carbon dioxide depends on the processes of the life activities of phytoplankton (photosynthesis and decay). Experiments with phytoplankton Sceletonema constatum (94) showed a lowering of electroconductivity in light and an increase in darkness accompanied by a change oh pH, oxygen and chlorine, (Figure 4). The experiments of K. Park (91) had the goal of defining electroconductivity changes caused by separate chemical parameters in processes of photosynthesis and respiration (Figure 5).

FIGURE 2



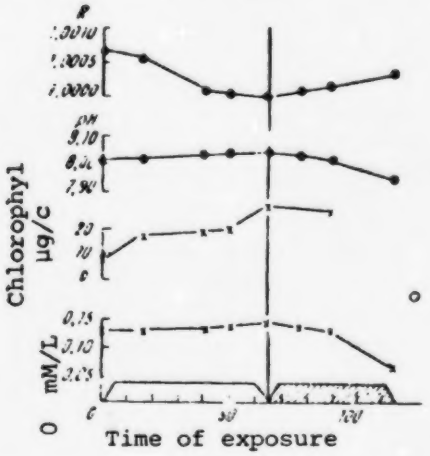
Changes of relative electroconductivity of sea water with changes of content of pH, HCO_3^- and CO_3^{-2} from (93).

FIGURE 3



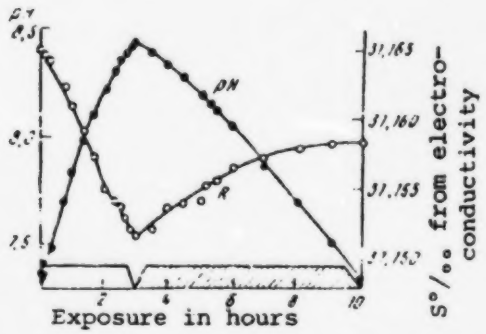
Changes in relative electroconductivity of sea water with changes in CO_2 after (95).

FIGURE 4



Changes in parameters of experiments with plankton growth in water Sceletonema costatum from (94).

FIGURE 5



Changes in electroconductivity and pH by photosynthesis and respiration from (91).

Exposed to light, electroconductivity is lowered by 0.04% (approx. 0.013 °/₀₀). From this value 0.02% is due to bicarbonate-to-carbonate transformation; 0.01% is due to produced oxygen; the remaining 0.01% is assumed to be associated with consumption of other biogenic elements. A relatively reliable fraction is associated with the consumption of nitrates (.002%), but suitable contribution of other biogenic elements was not successfully accounted for.

For the reaction in darkness electroconductivity increased only 0.02% although pH came back to the beginning situation. This increase conformed only to observed values of transformation of carbonate into bicarbonate. Use of oxygen and regeneration of biogenic elements was not reflected on the values of electroconductivity. This shows the lack of time for a full regeneration of biogenic elements and corresponding decrease of oxygen content.

In this way, at the present time it is clear that the saline content of the waters of the world's oceans undergo variations connected with the river runoff and the corresponding nature of water masses, with processes of ice formation and melting, biogenochemical processes (life activity of organisms and processes of slow decay of their residues), and ion exchange with suspended load and precipitation.

Hydrostatic pressure has a definite effect on 'apparent' concentration and activity of ions as seen in the distribution of forces of gravity.

Consequently the above definitions of salinity being based on assumption of the constant composition of sea water are not identical which causes difficulties in comparing results of the different researchers.

The work for determining the errors of conductiometric methods in definitions of salinity showed that measurement of electrical conductivity takes into account exchange of some ions for others and gives a more exact representation of the total composition of dissolved matter. Because of this, the definition for electroconductivity salinity gives more exact results than chlorinity methods; the tie between electroconductivity and salinity is closer than between chlorinity and salinity. This is experimentally shown in the work of the program workers group for standardizing the constitution of sea water (8).

DEFINITION OF SALINITY FROM CHANGES OF ELECTROCONDUCTIVITY, TEMPERATURE AND PRESSURE

The dependency of electroconductivity of sea water on salinity

Electroconductivity caused by dissolved electrolyte is connected with many physiochemical properties of the dissolved substance and the solvent. This connection is characterized by the classical equation of Debye-Huckel:

$$c = \Sigma \frac{n_m z_m \cdot e}{6\pi\eta} \cdot \left[\frac{1}{a_m} - \sqrt{\frac{4\pi e^2}{DKT_k}}\right] \cdot \sqrt{\Sigma n_i - z_i^2} \qquad [9]$$

where n_m = number of ions, m - type; per cm^3

C = relative electroconductivity

a_m = radius of ion type m

Z_m = valency of ion type m

D = dielectric constant of solution

K = constant (Boltzmann)

T_k = temperature °K

n_i = number of ions i - type per cm^3 (these ions from the ionic atmosphere for ion m - type)

Z_i = valency of ion type i

e = the charge of electrons

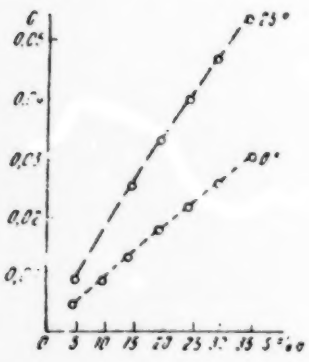
η = viscosity of electrolyte

As can be seen the formula is complicated enough even for a mono-electrolyte (in the given circumstance of a strong one). Sea water can be called the most complicated mixture of electrolytes. Furthermore equation [9] characterizes electroconductivity as its infinite dilution value where ion-ion interaction is not important. Sea water salinity of about 35 $^{\circ}/_{\circ\circ}$ appears to be a solution of average concentration; in the equation describing its electroconductivity there must be terms characterized by the interaction of ions. Because of this, application of the classical law of activity to sea water would be unsuitable (15, 19), and its electroconductivity is described by systems of complicated equations. Naturally, the calculation of influence of changes of temperature and pressure bring further complication to the mathematical dependence. At the same time by the corroboration of Horne, supported by the experimental data, "the system (sea water) is so complicated and contains so many separate parts, that its complexity and diversity 'extinguishes itself' and becomes or appears to be a phenomenological simplicity". As a result of this, some parts of this theory and its model are applicable to sea waters. However a mathematical description of electroconductivity of sea water with its physiochemical properties is still far from being accomplished.

In oceanology there have been built empirical relationships and appropriate tables have been developed between electroconductivity and basic parameters: salinity, temperature, pressure.

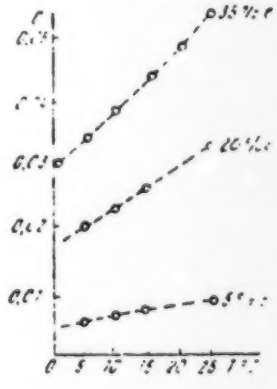
The complexity and non-unique character of the links between salinity and electroconductivity are illustrated by curves in Figures 6, 7 and 8. The form of these curves shows the character of the links C-S as a function of changes of temperature and to a lesser extent of salinity.

FIGURE 6



The dependency of electroconductivity of sea water on salinity from (16, 17)

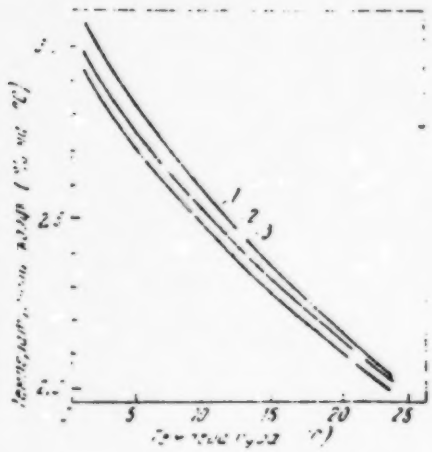
FIGURE 7



The dependency of electroconductivity of sea water on temperature from (15, 16)

The first attempt to clarify the relationship of salinity-electroconductivity was by Ruppin in 1905 (106), for samples gathered in the Baltic and Mediterranean Seas. The conductivity was measured with the help of a primitive conductometer with a telephone earpiece null indicator. Formulae were derived connecting salinity and electroconductivity with the effects of temperatures coming in tables by Krummel (73) and later in tables of Zubov (7). These formulae used in the application of the techniques of that time gave uncertainties of 0.1 °/$_{oo}$, much less accurate than titrometric methods.

FIGURE 8



Temperature coefficients of electroconductivity of sea water as functions of temperature and chlorinity from (93). The curve 1 is 1 Cl°/$_{oo}$, the second curve is 10 Cl°/$_{oo}$, the third curve is 19 Cl°/$_{oo}$.

In the 1930's with the use of improved salinometer, Thomas Thompson and Utterback (113) obtained formulae connecting electroconductivity and chlorinity for water taken from different depths of the Pacific and Indian Oceans and Mediterranean Sea.

$$0°C;\ C = 1.7875\cdot10^{-3}Cl - 2.9596\cdot10^{-5}Cl^2 + 1.127\cdot10^{-6}Cl^3 - 1.902\cdot10^{-}\ Cl^4$$

$$5°C;\ C = 2.0818\cdot10^{-3}Cl - 3.6859\cdot10^{-5}Cl^2 + 1.449\cdot10^{-6}Cl^3 - 2.520\cdot10^{-}\ Cl^4$$

$$10°C;\ C = 2.3749\cdot10^{-3}Cl - 4.1334\cdot10^{-5}Cl^2 + 1.554\cdot10^{-6}Cl^3 - 3.829\cdot10^{-8}Cl^4$$

$$15°C;\ C = 2.7009\cdot10^{-3}Cl - 5.1390\cdot10^{-5}Cl^2 + 2.097\cdot10^{-6}Cl^3 - 3.829\cdot10^{-8}Cl^4$$

$$20°C;\ C = 3.0191\cdot10^{-3}Cl - 5.6253\cdot10^{-5}Cl^2 + 2.181\cdot10^{-6}Cl^3 - 3.804\cdot10^{-8}Cl^4$$
$$25°C;\ C = 3.3524\cdot10^{-3}Cl - 6.2481\cdot10^{-5}Cl^2 + 2.371\cdot10^{-6}Cl^3 - 4.049\cdot10^{-8}Cl^4$$

The values of electroconductivity, calculated by these formulae corresponded with experimental definitions to an exactness 1.10^{-5}mho/cm, a value of chlorinity to 0.02 °/₀₀ in the interval 5 to 20 °/₀₀; for higher chlorinities, the error is somewhat greater. At the same time in Berlin University analogous researches (27) were carried out using samples from the Red and Mediterranean Seas and the Central Atlantic.

For a long time the data of Thomas et al were universally accepted. In spite of this Pollack (100) had some doubts of the exactness of these data. He considered that the value of electroconductivity bearing on the solution KCl and the cell constant were defined inexactly. However a checking of the data by Cox (41) showed that in the region of 33 to 35 °/₀₀ the data of Thomas et al agreed with his exact measurements and errors appeared only in the region of the highest salinity. The results of Thomas et al at higher salinities were lower than the results of Cox. The values of error were approximately equal 0.013 °/₀₀ at salinities of 36 °/₀₀ and 0.093 °/₀₀ salinity of 39 °/₀₀. Cox came to the conclusion that the equations of Thomas et al were applicable only at chlorinities lower than 19.3 °/₀₀.

To check the data of Thomas et al Weyl (123) carried out a series of experiments and attempted to calculate the temperature dependence of electroconductivity and chlorinity values. He produced the empirical formula for ranges Cl = 17-19°/₀₀ at T° = 0-25°C;

$$\log C = 0.57627 + 0.892 \log Cl - 10^{-4}\cdot(25-T)\cdot\{88.3+0.55(25-T) + 0.0107(25-T) - Cl[0.145 - 0.002(25-T) - 0.0002(25-T)^2]\} \quad [10]$$

Electroconductivity calculated by this equation is different from the data of Thomas et al by less than 0.1‰.

By the 1960's conductometric technology had so improved that the question was raised about defining salinity to the third decimal point and making more precise the relationship between conductivity salinity and temperature (31-37, 38, 115, 116). At this time many researchers rejected conductance-type salinity instruments replacing them with inductive ones (10). The conductivity of waters of salinity different from normal sea water is expressed nondimensionally as; the ratio of electroconductivity of water salinity S to electroconductivity in water salinity 35.000 °/₀₀.

To examine the relationship of electroconductivity/salinity/temperature a special work group of experts in oceanographic tables and standards was formed. The result of the program was the publication of the new International Oceanographic Tables and a recommendation of acceptance of conductometric methods as the standard method of defining salinities (118).

The application of inductive electroconductivity sensors in situ facilitated the automation of research with the aid of immersed CTD sondes.

There then appeared the need to derive corresponding corrections because of the effect of the in situ measurement of the temperature, pressure and electrical conductivity. Various researchers have tried to construct a relatively uncomplicated mathematical transformation using aforementioned relationships between values S, C, T, P, and relating the measured values of electroconductivity, temperature and pressure to the standard equation for the electroconductivity ratio R_{15} for 15°C and atmospheric pressure.

Relationship of dependencies R_{15} to temperature and relative electroconductivity at an arbitrary temperature is expressed by the equation:

$$R_{15} = y^1(T, R_T) \qquad [11]$$

where relative conductivity at 15°C is defined as:

$$R_{15} = \frac{C(S,15,0)}{C(35,15,0)} \qquad [12]$$

where C(S,15,0) - specific electroconductivity of sea water with salinity S at temperature 15°C and atmospheric pressure 0 db. and C(35,15,0) - specific electroconductivity of normal sea water at temperature 15°C and 0 db.

Relative electroconductivity of sea water at temperature T, salinity S and hydrostatic pressure 0 db is defined as:

$$R_T = \frac{C(S,T,0)}{C(35,T,0)} \qquad [13]$$

where C(S,T,0) - specific electroconductivity of sea water with salinity S at temperature T and hydrostatic pressure 0 db; and C(35,T,0) - specific electroconductivity of normal sea waters at temperature T and hydrostatic pressure 0 db.

The calculation of the values of pressure effects between R_T and relative electroconductivity R_{TP} at pressure P is from;

$$R_T = \phi(R_{TP}) \qquad [14]$$

where

$$R_{TP} = \frac{C(S,T,P)}{C(S,T,0)} \qquad [15]$$

C(S,T,P) - specific electroconductivity of sea water with salinity S at temperature T and hydrostatic pressure P. R_{TP} is a function of pressure, temperature and salinity:

$$R_{TP} = f(P,T,S) \qquad [16]$$

By equation [16], equation [15] is transformed to:

$$C(S,T,0) = \frac{C(S,T,P)}{f(P,T,S)} \qquad [17]$$

and with formula [13] we get:

$$C(S,T,0) = R_T \cdot C(35,T,0) \qquad [18]$$

Combining equations [17] and [18] gives:

$$R_T = \frac{C(S,T,P)}{f(P,T,S) \cdot C(35,T,0)} \qquad [19]$$

Dependency of specific electroconductivity of normal sea water on temperature is written in the form:

$$C(35,T,0) = C(35,15,0) \cdot Y(T) \qquad [20]$$

Substitution of equation [20] in equation [19] gives a generalization of the formula, connecting R_T with changes in electroconductivity:

$$R_T = \frac{C(S,T,P)}{C(35,15,0) \cdot Y(T) \cdot f(P,T,S)} \qquad [21]$$

In this way, knowing the function Y(T), f(P,T,S) and the value C(35,15,0) it is possible from the in situ value of specific electroconductivity R_T and by further use of equation [11] to find the relative electroconductivity R_{15} at temperature 15°C. This is done by using the UNESCO tables where the data is transformed for a fixed value of temperature and pressure = 1 atm. and also by comparison of data from CTD sondes and laboratory salinity measurements. Experimental and some theoretical research has allowed definition of the above mentioned relationships and values. First we will examine most widely used and accurate relationships in detail.

In the first place we will establish that equation [8] linking salinity of sea water with electroconductivity does not appear to be natural. Brown and Allentoft (30) in their experiments over ranges of salinity 0-50°/$_{oo}$ composed six polynomials relation R, S°/$_{oo}$ and T° for various subranges of salinity. (Unfortunately we were not able to obtain copies of all the papers' references in (30)). For ocean ranges their polynomials were adjusted by Jaeger (101) to make $R_{15} = 1.0$ for S = 35°/$_{oo}$. This then gave:

$$S = -0.21977 + 29.81964R_{15} + 7.95554R_{15}^2 - 3.88602R_{15}^3 + 1.56530R_{15}^4 - 0.23469R_{15}^5 \qquad [22]$$

Bisset-Berman (112) for ranges of salinity 20-51°/$_{oo}$ developed the polynomial:

$$S = -0.28073 + 30.29562R_{15} + 6.73684R_{15}^2 - 2.48100R_{15}^3 + 0.80896R_{15}^4 - 0.07944R_{15}^5 \qquad [23]$$

Besides this they derived equations for ranges of 0-20°/$_{oo}$ and 51-60°/$_{oo}$. Calculations of S by equations [8] and [22] in ranges R_{15} from 0.2 to 1.2

gives root mean square deviations of 0.002°/$_{oo}$ with maximum error of 0.009°/$_{oo}$ at R_{15} = 1.15 (41°/$_{oo}$) and 0.005°/$_{oo}$ at R_{15} = 0.85 (29°/$_{oo}$).

Cox (41) explains these differences by noting that his samples as opposed to the samples of Brown and Allentoft were natural as the samples of lower salinities consisted of ocean water diluted by river water while samples of Brown and Allentoft were diluted by distilled water. The values of electroconductivity derived by Cox at the same chlorinity were somewhat higher. Different values of the coefficient "a" (a = 0.03°/$_{oo}$ in formula of Knudsen (1)) relate to a characteristic degree of mineralization of the diluting water. If Cox had used samples diluted with sea water shown in Table 1 then his differences to the data of Brown and Allentoft could have reached values close to the known coefficient "a" characteristic for the regional waters which were used for dilution. In this regard the opinion of the authors (23) is that equations [8] and [22] are not appropriate for application in regions where the water is influenced by continental runoff or with anomolous waters with a significant variation in ionic composition is very appropos!

The equations above express the dependency of salinity upon relative electroconductivity R_{15}.* However both in laboratory and especially in ocean situations it is not always possible to measure relative electroconductivity at 15°C. Because of this corrections are necessary to allow for deviations of temperature of the samples from 15°C.

Changes of relative electroconductivity of seawater with temperature

The influence of temperature on relative conductivity of sea water was found by Cox (41) et al, and Brown and Allentoft (30). Cox and others proposed the correction $\Delta_{15}(T) = R_{15} - R_T$ for obtaining the relative electroconductivity at 15°C from relative electroconductivity at temperature T. The formula was derived in the following way. For each of eight samples which had at 15°C the approximate relative conductivities 0.1; 0.4; 0.5; 0.7; 0.8; 0.9; 1.0; 1.1; and 1.2 R_T was subsequently measured at eight values of temperature from 14-29°C at atmospheric pressure. The results of the measurement were embodied in equation:

$$R_T = R_{15} + K_1(T - 15) + K_2(T - 15)^2 \qquad [24]$$

giving the best relationship between the values and temperatures of coefficient K_1 and K_2 for each sample. K_1 and K_2 themselves appear as functions of R_{15} with that feature that they approach K"0" when R_{15} is close to 0.0 or 1.0. In order to find the dependency K_1 and K_2 from R_{15} graphs were constructed of the link:

$$R_{15} - K_1/R_{15}(R_{15} - 1)$$

$$R_{15} - K_2/R_{15}(R_{15} - 1)$$

The graphs were approximated by equations of the second order:

$$\frac{K_1}{R_{15}(R_{15} - 1)} = 96.7 - 72.0\,R_{15} + 37.3\,R_{15}^2 \qquad [25]$$

* All the above relationships of salinity to electroconductivity were derived by Cox at 20°C

$$\frac{K_2}{R_{15}(R_{15} - 1)} = 0.63 + 0.21\,R_{15}^2 \qquad [26]$$

By substituting equations [25] and [26] in equation [24], the unknown quantity was defined as the interconnection of R_{15}, R_T and T. Empirically it was found that R_{15} could be reasonably substituted for R_T. Such a substitution in the calculation for $\Delta_{15}(T)$ and in indicated ranges does not give a significant error. The final form adopted for R_{15} was:

$$R_{15} = R_T + R_T(R_T - 1)(T-15)[96.7 - 72R_T + 37.3R_T^2 - (0.63 + 0.21R_T^2)(T-15)]\cdot 10^{-5} \qquad [27]$$

Formulae were fitted by Cox et al over the ranges of temperature 10-30°C.

Brown and Allentoft (30) for ranges of temperature 0-30°C proposed another formula:

$$R_{15} = R_T = R_T(R_T - 1)(0.0175 - 0.0045R_T)\cdot(-1 + 0.08T - 8.9\cdot 10^{-4}T^2) \qquad [28]$$

Jaeger (61) proposed a generalization of the formula equation [27] and [28]:

$$R_{15} = a_1R_T + a_2R_T^2 + a_3R_T^3 + a_4R_T^4 \qquad [29]$$

where coefficients are found in equations:

$$a_1 = b_0 + b_1T + b_2T^2$$

$$a_2 = b_3 + b_4T + b_5T^2$$

$$a_3 = b_6 + b_7T + b_8T^2$$

$$a_4 = b_9 + b_{10}T + b_{11}T^2$$

From Ccx and others (41) values of coefficient b_i are equal to:

$b_0 = 0.0159225$ $\qquad$ $b = 0.0168675$

$b_1 = -0.1156000\ 10^{-2}$ $\qquad$ $b_7 = -0.1156000\ 10^{-2}$

$b_2 = 0.6300000\ 10^{-5}$ $\qquad$ $b_8 = 0.2100000\ 10^{-5}$

$b_3 = -0.0267225$ $\qquad$ $b_9 = 0.0060675$

$b_4 = 0.1876000\ 10^{-2}$ $\qquad$ $b_{10} = 0.4360000\ 10^{-3}$

$b_5 = -0.6300000\ 10^{-5}$ $\qquad$ $b_{11} = -0.2100000\ 10^{-5}$

From the definition of Brown and Allentoft these same coefficients (b_i) are equal to:

$b_0 = 1.0175$ $\quad b_5 = -1.9580\ 10^{-5}$

$b_1 = -0.1400\ 10^{-2}$ $\quad b_6 = 0.0045$

$b_2 = 1.5575\ 10^{-5}$ $\quad b_7 = -0.0360\ 10^{-2}$

$b_3 = -0.0220$ $\quad b_8 = 0.4005\ 10^{-5}$

$b_4 = 0.1760\ 10^{-2}$ $\quad b_9 = b_{10} = b_{11} = 0$

Jaeger (61) finds from the comparison of values R_T calculated by equations [27] and [28] in ranges of relative electroconductivity from 0.2 to 1.2 and temperatures from 10 to 30°C a root mean square rms deviation of 0.002 °/₀₀ with maximum error at R = 0.60 of 0.005 °/₀₀ (20°/₀₀, 25°C) and 0.007°/₀₀ (20°/₀₀, 10°C) in a calculation of salinity. In this temperature range but with a lesser range of electroconductivity (0.85-1.15), the root mean square deviation was 0.0007°/₀₀ with the largest deviation of 0.003°/₀₀ at R_T = 0.85 (29°/₀₀, 10°C). Jaeger (61) recommends using equation [27] in a laboratory situation in lower ranges of temperature and equation [28] in conditions of in situ at higher ranges of temperature.

To the small number of theoretical works on the connection between salinity and specific electroconductivity a place belongs for the work of Accerboni and Mosetti (25) who did research on the ranges of salinity and temperature 0 to 40°/₀₀ and 0 to 30°C.

The authors put forth the formula:

$$C = \left(2.1923 + 0.12824 \cdot \frac{T^{1.032}}{1 + T^{0.032}}\right) \cdot \frac{S}{1 + S^{0.1243}} \cdot \qquad [30]$$

$$\cdot\ e^{-0.000978S} \cdot e^{-0.0000165(S - 35)(T - 20)}$$

They tried theoretical analysis and put forth the formula including nine empirical constants to fit the experimental data of Cox, Brown and Allentoft. Comparison of values of salinity calculated by equation [30] and the equations of Cox et al (in ranges of 10 to 30°C and 0 to 40°/₀₀) carried out by authors (121) gives maximum deviation of 0.003°/₀₀ at 40.196°/₀₀ and 25°C. Comparison of values derived by equation [30] referred to data of Brown, Allentoft gives maximum deviation of 0.079°/₀₀ at 15.468°/₀₀ and 0°C. Similar differences are found in exactnesses of theoretical considerations by authors (25) and also the differences between experimental data and situations in the basic definition of the nine constants.

Changes of specific electroconductivity of normal water with temperature

Since normal water appears to be at present the only standard used in calibration of salinity, a definition of its features is essential both from a theoretical and a practical point of view. In basic research of the

last 10 years studies of temperature dependencies of electroconductivity of normal waters depended on the measurements of relative electroconductivity since it could be measured more exactly than absolute specific conductivity and an absolute value of specific electroconductivity of normal waters at 15°C and atmospheric pressure.

Brown and Allentoft (30) having conducted experimental works made up a table and equations describing the dependency of relative electroconductivity of normal waters on temperatures, the coefficients were adjusted so that relative electroconductivity R_{15} at 15°C was equal to 1.0.

$$R(T) = 0.67654668^{*} + 0.020131661T + 0.99886585\cdot10^{-4}\cdot T^{2} - 0.19426015\cdot10^{-6}\cdot T^{3} - 0.67249142\cdot10^{-8}\cdot T^{4} \quad [31]^{*}$$

where

$$R(T) = \frac{C(35,T,0)}{C(35,15,0)}$$

Root mean square deviation of values expressed by formula [31] from experimental data were 0.000002 (0.003°/$_{oo}$ in equivalent salinity).

The other equation is proposed by Perkin and Walker (96). It is derived on the basis of experimental data of Brown and Allentoft, a value of specific electroconductivity of normal water at 0°C taken from the work (103). For ranges of temperatures 0 to 25°C formula from (96) is:

$$C(35,T,0) = 29.03916(1 + 0.0297175T + 0.00015551T^{2} - 0.000000789T^{3}) \quad [32]$$

Knowles (69) proposed formula for ranges of temperature 0 to 40°C (his formula fitted experimental data of Reeburgh (103)):

$$C(35,T,0) = 29.04433 + 0.86141\cdot T + 0.46109\cdot10^{-2}T^{2} - 0.254\cdot10^{-4}\cdot T^{3} \quad [33]$$

Knowles also proposed two formulae of temperature dependence for water of the Red Sea (Cℓ = 19.374°/$_{oo}$ and C = 42.904) and normal waters (Cℓ = 19.372°/$_{oo}$ and C = 42.917 mmho/cm). A comparison of values from the equation of Knowles and formula [32] gives root mean square deviations of 0.001 mmho/cm, comparisons with formula [33] and [32], 0.0013 mmho/cm, and 0.00212 mmho/cm from comparison of formula [32] and the two other formulae of Knowles.

The research into changes of specific electroconductivity with temperature is always divorced from the question of values of specific electroconductivity of normal waters at 15°C (or at other fixed temperatures), and also the necessity of solving the question of whether normal water should be used as the standard for electroconductivity as it is for chlorinity.

---

*In the work (112) the first member of the polynomial [31] = 0.676524.

Normal water - supporting standards of salinity

In defining salinity by relative electroconductivity the standard for calibration of salinometers should be normal sea water, that is water with salinity of 35 °/₀₀ at 15°C and atmospheric pressure. Under these conditions relative electroconductivity of normal sea water is taken as 1.0.

At the present time International Standards normal water is prepared in Copenhagen as specified by Knudsen. The Copenhagen standard is now in use in 47 countries of the world (63) - more than 18000 ampoules per year.

In use in the USSR since 1955 is a normal water which in quality does not yield to that of the Copenhagen as corroborated by multiple verifications (14). The introduction of the Soviet normal water was organized on the initiative of L.A. Zankevich under auspices of the laboratory of normal water AANII (now the analytic laboratory IOAN of the USSR). The introduction of the normal water was under the leadership of a group of specialists consisting of L.K. Blinova, M.P. Nesterov, M.V. Fedosova, N.E. Chigirina and headed by S.N. Bruevich. The laboratory carried out research on normal water in the USSR and exports it to several foreign countries.

Normal water is prepared from filtered sea waters taken in the Atlantic Ocean from the surface. The salinity is brought to 35 °/₀₀ by diluting sea water with distilled water (116). We note that use of normal waters as the standard of conductomeasures, is increasing. The authors below noted the necessity of maintaining identical isotopic composition of base water and the distilled water dilutant (37, 43, 63, 89). A specialized method of preparing distilled waters from sea water is proposed in (42).

The method of preparing normal water assumes maximum cleaning from the water of impurities, preventing settlement of sediment, and getting rid of air bubbles when sealing the ampoules and in further manipulation of the water (for example, calibration of salinometers). For decontamination, the water is heated to 27°C before pouring.

The requirement of maximum cleanliness of a standard includes minimum weight of dissolved organic matter, observation of identical saline content and a predetermined place of collecting the base sea water - the Bay of Biscay*. The salinity of waters of the Bay is close to 35°/₀₀, the water is oligotrophic and contains little suspended matter.

However these measures do not fully preclude the possibility of a variation of the composition of the standard, since measurements of values of electroconductivity of waters with equal chlorinity vary in the ranges from 42.698 to 42.929 mmho/cm. In Table 12 are shown the values of absolute electroconductivity of normal waters from the data of different authors.

Such variations in value of specific electroconductivity of normal waters can cause significant errors in the use of any formulae connecting salinity, electroconductivity, temperature with an instrument, calibrated to noncorresponding values #(35,15,0). Example of errors are shown in Table 13 (120).

* Some national standards are prepared from waters taken from the location closest to the coast of the country concerned with that ocean.

TABLE 12

Electroconductivity C(35,15,0)mmho/cm	Researchers accepting the data value of C(35,15,0)	Literature Sources
42.896*	Cox, Brown-Allentoft, Weyl	61,121
42.923	Perkin-Walker, Reeburgh	96,103 120,121
42.907 42.904 42.917	Knowles	69
42.899	Rhode	120,121
42.918 (42.917)**	Ribe-Howe	120,121
42.929	Bennett	120,121
42.905 (42.902)**	Accerboni-Mosetti	120,121
42.913	Pritchard	120,121
42.698	Daniel-Collias	120

* from data of (69) this value is close to 42.923
** corrected values

TABLE 13

Salinity (°/$_{oo}$) calculated by formulas with the use of data: C(35,15,0) = 42.80 mmho/cm; T = 15, 0°C; P = 0db	
Perkin-Walker	34.887
Rohde	34.910
Ribe-Howe	34.893
Bennett	34.882
Accerboni-Mosetti	34.906
Pritchard	34.897
Daniel-Collias	35.095
Zaburdaev et al	34.912

It is recommended in (40) that both the value of chlorinity and the value of electroconductivity be shown on the ampoules of normal water.

In 1962 the combined work group of UNESCO accepted the solution of certifying normal waters as to electroconductivity; however up until this time this has not been done.

For a checking of the influence of possible variations of saline composition of different normal waters Park (89) compared salinities defined by electroconductivity with salinities found by chlorinity written down on labels for 12 series of Copenhagen water with times of storage from seven months to 26 years. In the experiment he used Australian inductive salinometers.

The salinity of nine series of the 12 corresponded in the limits of 0.004 $^{\circ}/_{\circ\circ}$, and 3 series showed deviations of 0.006; 0.012; 0.017$^{\circ}/_{\circ\circ}$. On the basis of these results, Park came to the conclusion that normal water gives a good relative agreement of salinity of different series and that Copenhagen sea water can be a standard of electroconductivity just as of chlorinity. Analogous checking for Soviet normal sea water was carried out on 53 series with times of storage from one month to 16 years. It should be noted that all definitions of electroconductivity and chlorinity at preparation of normal Soviet sea waters are carried out in relation to Copenhagen normal waters. An overwhelming majority of points (about 85%) came within the limits of precision of the experiment. The maximum deviation - 0.010$^{\circ}/_{\circ\circ}$ salinity - was shown by one sample, two had deviations of 0.008-0.009$^{\circ}/_{\circ\circ}$ and the rest were within limits of 0.005-0.006$^{\circ}/_{\circ\circ}$. In addition a comparison was made of salinities found by electroconductivity for some of the same series. The root mean square deviation was $\pm$0.002$^{\circ}/_{\circ\circ}$, deviation not exceeding $\pm$0.005$^{\circ}/_{\circ\circ}$ composed 93% of cases and only 7% had deviations greater than 0.006-0.007$^{\circ}/_{\circ\circ}$. An attempt to investigate the possibility of errors of normal water in the process of pouring out showed no systematic deviation in the end and beginning phases of preparation of the samples of any series. The deviation of salinities of the individual ampoules from the average of 95% of cases did not exceed 0.005$^{\circ}/_{\circ\circ}$. The authors (14) came to the conclusion that the Soviet normal waters are stable over time within a series both as to chlorinity and as to electroconductivity.

In order to reduce the use of expensive normal water, Morcos and Riley (82) carefully investigated theory and practice of making sub-standard waters. Such auxiliary water may be used for daily or more frequent calibrations. Lewis and Sudar (75) consider that for calibration of STD sondes with automatic temperature compensation it is essential to have substandard sea water made by way of weight dilution of normal sea water with distilled water; salinity will be close to the salinity of the sample in question. By using such substandard water, they were trying to obtain the incorporation of a temperature correlation with accuracy of $\pm$0.01°C in ranges $\pm$3°C. Evidently for making substandard waters it is possible to employ water taken from a region of research and first calibrated by normal waters. The advantage of substandard water comes from the correspondence of its ion composition to the sample in question. It opens the possibility of widening the range on temperature correction and lowers the error in salinity connected with the difference in the saline composition in question in normal waters.

Effect of pressure of electroconductivity of sea water

With the conductometric definition of salinity and measuring in situ, the knowledge of the increase of electroconductivity of sea water with the increase of hydrostatic pressure is essential. In comparing the data from the literature Horne (19) concluded that in the range of interest for oceanography, pressure changes the value of electroconductivity of sea water by not more than 12%.

The active mechanism of pressure effects on electroconductivity of sea water has not been investigated very thoroughly and the data from the literature is contradictory.

One of the main reasons for the increase of electroconductivity with increase of pressure is the increase of concentration of particles in a unit of volume on account of the compression of the water. In Figure 9, illustrating the effects of different factors in variation of electroconductivity withpressure, the factor of the compression of the water is characterized by a curve #1. The next by degree of influence (curve #2) is the decrease of viscosity at increase of pressure. This is connected with anomalous feature, the existence of water complexes, which are broken down at high pressure, bringing the water to its usual, unassociated liquidity. Another noteworthy factor is the increase in the degree of dissociation of weak (and also evidently average strength) electrolytes. In particular this concerns $MgSO_4$ whose contribution to the sum of electroconductivity is approximately 3% (19, 58). The influence of the dissociation of magnesium sulfate on electroconductivity is shown in curve line #3. These three effects do not compose all effects on electroconductivities. The curves lying lower than curve #4 characterize the experimentally derived dependencies.

Up until the present there have been relatively few attempts to investigate the effect of pressure on conductivity of sea waters. One of the first, the experiments of Hamon (56), defined average changes of electroconductivity at the deviationof pressure of 1,000 dbars at several values of temperature, of water with chlorinity at 19.7°/$_{oo}$. Hamon estimates the accuracy of his results at ±5% corresponding ±0.02% in salinity. Horne and Frysinger (59) defined changes of electroconductivity of sea water with Cℓ - 9.68, 17.61 and 19.376°/$_{oo}$ at temperatures 0, 5, 15 and 25°C over ranges of pressure from 10 to 13800 dbar. They proposed the following equation for the dependency of electroconductivity on pressure:

$$C_p = C_o + [(0.35\pm0.25) + (0.18\pm0.028)C\ell]10^{-6}P \qquad [34]$$

where C_p and C_o are the specific electroconductivities at pressure p and at 1 atm respectively.

Uncertainties in the given data are so great that using them for exact calculations is not possible. It is possible to look at them as a first approach to the calculation of electroconductivity at high pressures.

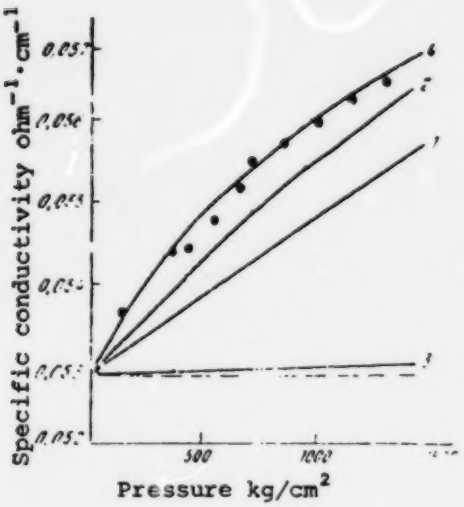


Figure 9: The effect of pressure on electroconductivity of sea water (at 25°C).
1. Calculation of compression of the water
2. Calculation of changes of viscosity
3. Calculation of increase of degree of dissociation of $MgSO_4$.
4. Experimental relationship.

The influence of pressure on electroconductivity of sea water was thus based on theories of electroconductivity and composition of solutions of sodium chloride as models of sea water (55). These researchers satisfactorily described only the largest effects and their results revealed significant divergences from experimental data.

Among the published works the fullest are the laboratory experiments of Bradshaw and Schleicher (28) which define the percentage increase of electroconductivity of sea water with increase of pressure at T° = 0, 5, 10, 15, 20 and 25°C, S = 32, 35, and 39°/$_{oo}$ over the range of pressure 0 to 10338 dbar higher than atmospheric. On the basis of their results they derived the formula:

$$\left[\frac{C(S,T,P)}{C(S,T,0)} - 1\right]\cdot 100 = \left[g(T)\cdot f(p) + h(p)\cdot j(T)\right] + \left[1 + J(T)\cdot m(S)\right] \quad [35]$$

where

$$f(p) = 1.042\cdot 10^{-3}p - 3.3913\cdot 10^{-8}p^2 + 3.3\cdot 10^{-13}p^3$$

(which describes the dependency of relative electroconductivity on pressure at 35°/$_{oo}$ and 15°C), and

$$g(T) = 1.5192 - 4.5302\cdot 10^{-2}T + 8.3089\cdot 10^{-4}T^2 - 7.9\cdot 10^{-6}T^3$$

(which describes changes with temperature of normal water),

$$h(p) = 4\cdot10^{-4} + 2.577\cdot10^{-5}P - 2.492\cdot10^{-9}P^2$$
$$J(T) = 1 - 1.535\cdot10^{-1}T + 8.276\cdot10^{-3}T^2 - 1.657\cdot10^{-4}T^3$$
$$I(T) = 6.95\cdot10^{-3} - 7.6\cdot10^{-5}T$$
$$m(S) = 35 - S^{\circ}/_{\circ\circ}$$

The exact correspondence of experimental data and results calculated by formula [35] gave at $\pm\ 0.005^{\circ}/_{\circ\circ}$ for accuracy of experimental data, $\pm\ 0.01^{\circ}/_{\circ\circ}$ for salinity. Jaeger (61) noted that equation [35] is used for the calibration of salinometers in situ. Ocean trials of instruments of different firms showed noticeable differences in calculations of salinity with calculated compensation of pressure. The errors in salinity were not constant and errors changed with depth: on the surface it was $0.0\ ^{\circ}/_{\circ\circ}$ deeper increased to $0.05^{\circ}/_{\circ\circ}$, from about 1700 m it remained the same to 3400 m, and then again diminished to $0.0^{\circ}/_{\circ\circ}$ at depths about 5100 m. As reasons the author of the article (61) proposed the following:

> "noncorrespondence of effect of pressure on electroconductivity of calibrated normal water and of natural water at depth, connected with the differences of their saline composition or other physiochemical properties; the error in measuring temperature; errors in calibration of the instruments; the inexactness of the formula".

Jaeger noticed that errors in temperature cannot be the reason for the observed errors in calculations of salinity since the salinity errors would necessitate temperature errors of $\pm\ 0.5°C$ while measurements were exact to $\pm\ 0.02°C$. In searching for other formulae Jaeger recommended concentrating attention on the reasons for divergences and care in interpretation of data from in situ instruments.

In conclusion it may be said that aspects of the effects of pressure on electroconductivity of sea water are still uncertain. The research on this question poses experimental difficulties, such that experiments can be carried out only in situ. Modelling the conditions of the depth, evidently causes errors, connected with the change of the physiochemical composition of sea water brought up from the depths; experiments with surface water also show unsatisfactory results.

METHODS OF CALCULATION OF SALINITY FROM SPECIFIC ELECTROCONDUCTIVITY WITH CORRECTIONS FOR TEMPERATURE AND PRESSURE

In previous sections we discussed the relationships of salinity S to relative electroconductivity at 15°C, relative electroconductivity from temperature $Y^1(T, R_T)$, specific electroconductivity of normal water from temperature y(T), specific electroconductivity on pressure f(P,T,S), and also the ambiguously defined values of specific electroconductivity of normal waters at 15°C. These relationships form the basis of all methods of calculation of salinity from specific electroconductivity, temperature and pressure. The variety of these relationships, the desire of the calculators to tailor process of calculating to the accuracy demanded by the problem and the precision of the measuring technology and the limiting of the range of values in the research regions has brought forth a large collection of these methods .

Overall these methods have in common the following set of calculations:

Calculating the value $R_T = \dfrac{C(S,T,P)}{C(35,15,0)\cdot Y(T)\cdot f(P,T,S)}$

by equation [16] and [20].

Calculating R_{15} by equation [11].
Calculating S by one of the equations giving $S = f(R_{15})$, will show the basic characteristics of the known methods, observed from (120, 121).

Method of Rhode

Valid for ranges $3.5 \leq T \leq 30°C$; $30 \leq S \leq 41°/_{oo}$, $0 \leq p \leq 7000$ dbar. Equation is an analytic approximation to data of Thomas et al, Bradshaw and Schleicher.

Method of Ribe-Howe

The accuracy of this method is $\pm 0.01°/_{oo}$ in ranges of $0 \leq T \leq 25°C$; $30 \leq S \leq 40°/_{oo}$; $0 \leq p \leq 700$ dbar. It is based on data of Cox et al, Brown and Allentoft, Bradshaw andSchleicher.

Method of Bennett

The accuracy of method $\pm 0.01°/_{oo}$ in ranges of $-2° \leq T \leq 30°C$; $0 \leq S \leq 40°/_{oo}$; a wide range of pressure. Making use of data of Cox et al, Bradshaw and Schleicher.

Method of Daniel-Collias

The accuracy of this method is $\pm 0.013°/_{oo}$ in ranges $0 \leq T \leq 30°C$; $10 \leq S \leq 35°/_{oo}$; $p = 0$ dbar. Equation is an analytic approximation to the data of Thomas et al.

The methods having the most applicatcn we treat in more detail.

Method of Perkin-Walker (96)

The method is valid for temperature and salinity values characteristic of Canadian Arctic waters. The exactness of the method $\pm 0.01°/_{oo}$ in ranges $5 < S < 40°/_{oo}$; $-2° \leq T \leq 20°C$; $0 \leq p \leq 1700$ dbar. Effects of pressure on specific electroconductivity f(P,T,S) is based on experimental data of Bradshaw and Schleicher and appears as a linear function of pressure

$$\frac{C(S,T,P)}{C(S,T,0)} = 1 + \frac{P}{49436 + 1567T + 21.33T^2 + 554.43C(S,T,P)} \qquad [36]$$

The maximum difference between the values calculated by this equation and data upon which it is based corresponds to an error in salinity of $0.01\ °/_{oo}$ (61).

The dependency of specific electroconductivity of normal waters on temperature and Y(T) is based on data of Brown and Allentoft, the value of C(35,15,0) is based on interpolation in experimental data of Reeburgh (103).

Calculated relative electroconductivity R_T uses relative electroconductivity R_0 at temperature 0°C by a formula based on experimental data of Brown and Allentoft for ranges of temperature 0 to 25°C:

$$R = R_T - \left\{6 + 380\sin\left[\frac{(R_T + 0.04)\pi}{1.03}\right] + 15\sin\left[\frac{(R_T + 0.04)3\pi}{1.03}\right]\right\} \cdot \cdot (0.0777T - 0.000454T^2 - 0.000018T^3)\cdot 10^{-5} \quad [37]$$

where R_T is found by substitution of equation [36] and [37] in equation [21].

From experimental data of Brown and Allentoft are found two equations linking R_0 with salinity of sea water for $0.40 \leq R_0 \leq 1.20$:

$$S = -0.5933 + 32.4822R_0 + 3.1106R_0^2 + 0.004\sin\left[\frac{(R_0 + 0.64)2\pi}{0.57}\right] \quad [38]$$

or where $0.14 \leq R_0 \leq 0.40$, equation [39] is appropriate:

$$S = -0.2166 + 30.686R_0 + 5.247R_0^2 \quad [39]$$

From the experimental data of Dauphinee a correction to salinity is derived which is essential to use in equations [38] or [39] for temperatures $1 \leq T \leq -2$°C:

$$\Delta S = \delta(-3.6 + 5.0T - 2.45T^2)\cdot 10^{-3} \quad [40]$$

where

$\delta = 1$ for $-2° < T < 1$°C,

$\delta = 0$ for $T > 1$°C

Method of Zaburdaev et al

The method allows the calculation of salinity with errors ± 0.01‰ in ranges 31 to 39‰ at temperatures 0 to 25°C and pressures 0 to 10000 dbar. Compensations for pressure effects uses the basic formula of Bradshaw and Schleicher (35). Dependency of specific electroconductivity of normal sea water Y(T), also the value C(35,15,0) are derived from data of Cox.

Zaburdaev and others proposed the following formula:

$$C(35,T,0) = 42.896[1.0 + 2.28649\cdot 10^{-2}(T-15) + 7.884\cdot 10^{-5}(T-15)^2 - 5.704\cdot 10^{-7}(T-15)^3 + 1.664\cdot 10^{-8}(T-15)^4] \quad [41]$$

As the equation connecting R_T and R_{15} and the relationship of S with R_{15} they used the polynomials of the International Oceanographic Tables of UNESCO (27, 8).

Salinity from measurements of electroconductivity, temperature and pressure of sea water is calculated in the following stages:

1. An approximate value is chosen, S*. In formula [35] S^* is but equal to 35°/$_{oo}$, then formula [21] is rewritten in the following way:

$$R_T^1 = \frac{C(S,T,P)}{C(35,T,0)\{1 + 0.01[g(T)\cdot f(p) + h(p)\cdot j(T)]\}} \qquad [42]$$

The difference between R_T^1 and R_T in the pressure range 0 to 10,000 dbar is not more than .28% for salinities in the range 31 to 39°/$_{oo}$ and temperatures in the range 0 to 25°C. (6)

Substituting in formulae [27] and [8] approximate values of R_T^1 and R_{15}^1 gives S*, differing from the true value by not more than 0.1 °/$_{oo}$.

2. After substitution of the approximate value, S*, in equation [35] formula [21] gives the exact value of R_T.

3. The exact value of S (salinity) is found by substituting the value of R_T in equations [27] and [8].

A simplified variant of the above means of calculation of salinity is found in the method worked out at MGI-AH-YCCP by B.V. Zaburdaev for hand and machine calculation of salinity from measurements of specific electroconductivity, temperature and hydrostatic pressure by the in situ sonde "Istok-3".

Preliminary evaluation by the author showed that errors calculated in relationship to the data for which it is worked out are less than ±0.02°/$_{oo}$ in ranges of salinity 10 to 42°/$_{oo}$, temperatures 02 to 30°C, pressure 0 to 2000 dbar.

For compensation of pressure effects equation [36] Perkin and Walker is used. Values, calculated by this equation, are different from the values calculated by equations ofBradshaw and Schleicher by not more than 0.01 °/$_{oo}$.

The following formula was proposed:

$$C(S,T,0) = C(S,T,P)\cdot\frac{49440 + 1570T + 21.3T^2 + 554.4C(S,T,P)}{49440 + 1570T + 21.3T^2 + 554.4C(S,T,P) + P} \qquad [43]$$

The dependency of specific electroconductivity of normal sea water on temperature derived from equations [32](Perkin and Walker) has the following form:

$$C(35,T,0) = 29.043(1 + 0.029624T + 0.00016145T^2 - 0.000000923T^3) \qquad [44]$$

Equations giving the ratio of electroconductivity R_T to ratio electroconductivity R_{15} and 15°C and linking R_{15} with salinity S used polynomials of International Oceanographic Tables 27 and 8.

Method of Fedorov

The method is valid for ranges $33 \leq S \leq 37\,^{\circ}/_{\circ\circ}$; $0 \leq T \leq 30$°C; and $0 \leq P \leq 2000$ dbar with errors $\pm 0.02\,^{\circ}/_{\circ\circ}$. The equation of compensation for pressure effects is based on experimental data of Bradshaw and Schleicher and is represented by linear dependency:

$$\frac{C/S,T,P/}{C/S,T,0/}$$

on pressure P. The maximum deviation between values calculated by this equation and the basic equation corresponds the error in salinity $\pm 0.005\,^{\circ}/_{\circ\circ}$ at salinity $35\,^{\circ}/_{\circ\circ}$ and $\pm .015\,^{\circ}/_{\circ\circ}$ at salinity 31 and 39 $^{\circ}/_{\circ\circ}$ for all ranges of pressure:

$$\frac{C(S,T,P)}{C(S,T,0)} = 1 + \frac{P}{100} \cdot [0.984 \cdot 10^{-3} + 0.269 \cdot 10^{-4}(15^0 - T) + 0.510 \cdot 10^{-6}(15^0 - T)^2] \qquad [45]$$

Changes of specific electroconductivity of normal sea water with temperature are based on the equation of Bradshaw and Schleicher (35) (value of specific electroconductivity of normal water C(35,15,0) is not shown). In ranges of temperature 5 to 25°C the value of salinity calculated by equation [45] and by the equation of Bradshaw and Schleicher differ by not more than $\pm 0.005\,^{\circ}/_{\circ\circ}$. Fedorov proposed the formula:

$$\frac{C(35,T,0)}{C(35,15,0)} = 1 - 0.2285 \cdot 10^{-1}(15^0 - T) + 0.8100 \cdot 10^{-4}(15^0 - T)^2 \qquad [46]$$

For mathematical reduction of the ratio R_T to ratio at 15°C (R_{15}) and the substitution of R_{15} in a salinity equation, polynomials [7] and [8] are used. The method presupposes the introduction of corrections $\Delta_{15}(T)$ only when salinity comes out in the limits of 33 to $37\,^{\circ}/_{\circ\circ}$.

Walker (120) and Walker andChapman (121) carried out a comparison of values of salinity, calculated by the above methods, and came to the conclusion that all methods are adequate near values of salinity of $35\,^{\circ}/_{\circ\circ}$ and temperatures of 15°C. For values of salinity different from $35\,^{\circ}/_{\circ\circ}$ and temperatures from 15°C, there appear to be a difference in the calculated value of salinity greater than at the values of T and S at 15°C and $35\,^{\circ}/_{\circ\circ}$.

It should be noted that all the methods are based on the principle of constant salinity composition of sea water. Furthermore as already has been noted the applicability of these relationships is limited in waters with lower salinities. Another source of error is extrapolation to wider ranges at S and T°. Thus, for example, the dependency of specific electroconductivity on pressure used is valid only in ranges of salinity 31 to $39\,^{\circ}/_{\circ\circ}$, the majority of authors extrapolate to any salinity.

The choice of method of calculation of salinity from specific electroconductivity, temperature, and pressure is closely connected with the question of calibration of salinometers and sondes.

THE ACCURACY OF CALIBRATION OF SALINOMETERS

The calibration of laboratory salinometers is usually carried out at the factory. In (75) the three bench salinometers which were tested were called by the authors A, B and C. A and C were manufactured in the U.S.A., B in Australia. The results are shown in Table 14.

TABLE 14

Salinometer	First sample °/₀₀	Second Sample °/₀₀	Third Sample °/₀₀
A	22.838	30.535	34.962
B	22.837	30.535	34.967
C	22.945	30.591	34.971

In spite of the fact that salinometers A and B were calibrated independently of each other, their indications correspond at the time when the sample C showed a divergence of 0.11 °/₀₀ at salinity approximately 22 °/₀₀. After a repetition of a calibration the error on salinometer C was eliminated.

Cox (38) carried out comparison of six laboratory salinometers (Table 15).

At salinity sample 35.149°/₀₀ differences do not exceed instrumental errors.

TABLE 15

Salinity by Cl °/₀₀	Salinity by measurement by salinometers °/₀₀					
	A	B	C	D	E	F
33.362	33.356	33.354	33.369	33.364	33.369	33.361
33.861	33.858	33.857	33.868	33.865	33.867	33.860
35.149	35.148	35.147	35.147	35.147	35.144	35.149
36.438	36.438	36.436	35.436	35.443	35.437	36.439
37.972	37.963	37.964	37.960	37.975	37.965	39.999*

* error because the samples were calibrated by extrapolated formula of Thomas et al (113), giving more errors at higher salinities.

A - salinometer of the National Oceanographic Institute Lab. in Wormley.

B - salinometer of the National Oceanographic Institute in Lowestoft.

C & D - samples of the Woods Hole Institute thermostatted at 25° and 15°.

E - salinometer from the University of Washington.

F - South African salinometer IMC.

For samples with other salinities, differences between instruments became greater when salinity samples deviated from 35 °/$_{oo}$. The results of the comparison showed that differences of measurement of different salinometers could attain 0,015°/$_{oo}$ at root mean square deviation 0.004 °/$_{oo}$. Park and Burt (92, 93) in comparing salinometers at the University of Washington with inductive salinometers found a constant value of deviation of 0.008 °/$_{oo}$ and root mean square deviation 0.003 °/$_{oo}$. In the opinion of the authors this constant error could be taken into account in calculations using normal water which is not standardized by electroconductivity.

In November 1963 the Oceanographic Service ONR of the USA carried out a controlled trial of 30 salinometers from 15 different laboratories and institutes (92). Eighteen inductive salinometers were tested, five salinometers of the University of Washington, four salinometers in NIO, two at Woods Hole Institute and one from Wenner, Smith, Soule, prepared by the US National Bureau of Standards.

The International Organization of Physical Oceanography (IAPSO) prepared three uniform samples with salinities 30, 35 and 39°/$_{oo}$. On each salinometer there were 10 measurements of each batch of samples. Determinations were carried out in one and the same day. The reproducibility was checked by twenty determinations of conductivity ratio of substandard (Table 16) (92).

TABLE 16

Factor of comparison	Salinity of control samples °/$_{oo}$		
	LOW	AVERAGE	HIGH
Base value of samples IAPSO	30.220	34.497	38.861
General average S by all salinometers	30.221	34.497	38.856
Average Minimum	30.205	34.488	38.346
Average Maximum	30.238	34.504	38.867
Difference between 3 & 4	0.033	0.016	0.021
Average deviation given separate salinometers from the value of IAPSO	±0.006	±0.004	±0.006
Average quadratic deviation	±0.0072	±0.0043	±0.0069

Testing of the salinometers showed that although the root mean square deviation was not great, separate measurements show significantly great differences.

On the basis of the evidence of intercalibration of the separate observers in 1973 the Working Group of UNESCO on Tables andStandards (119) came to the conclusion that the accuracy of the salinometers needed checking. The increase of errors of laboratory salinometers rated as ± 0.003 in ranges 2 to 42°/$_{oo}$ can result from aging of electronic design and changes of geometric parameters of the gauges.

It may be seen that differences in salinity measured on different salinometers may occur because of instrument error of the equipment. The most important cause for this evidently comes from the fact that the salinometers are calibrated, factory prepared, or precalibrated by users not dependent on each other and only at one point corresponding to salinity of 35°/$_{oo}$. Administrative measures of the International Service of Normal Waters in intercalibration of salinometers and introducing supplimentary standards of Baltic and Mediterranean waters should, in our opinion, have the attention of the interested organization.

In making measurements with the help of STD sondes the laboratory salinometer serves as a standard for statistical calibration of sondes. It is essential to be convinced of the reliability of one's own standard and correspondingly, in the comparison of the derived data with the results of other research.

A static calibration of sondes is carried out in laboratory situations. However with use of in situ instruments there is often a difference between results of measurement with the sondes and with the salinometers. A summary work (5) gives a broad comparison of Bissett-Berman 9006 and 9040 sondes with a lab. salinometer, carried out in the Mediterranean Sea in RRS "Discovery". Differences were noted between the sondes and salinometers which were connected with depth. The appearance of deviations from a series of stations was insignificant except when changing from one group of stations to another group. The authors (5, 32, 108) come to the opinion that the appearance of such deviations will necessitate calibration of the sondes by use of the salinometers when moving from station to station.

This method concludes with the suggestion that on each hydrographic station two stable layers should be chosen. It is desirable that one be close to the surface and the second at a near maximum depth of the sonde. In each of the layers measurements are made by immersed instruments and samples are taken by which the salinity is determined on the laboratory salinometer. From the results the STD sonde is corrected.

As an example the data of (75) shows a calibration of STD sondes using a laboratory salinometer. The rated data of the sondes: error in salinity ± 0.01 and in temperature ± 0.003°C. A comparison of salinity is shown in Table 17.

TABLE 17

Measurement of Sonde S°/$_{oo}$	Measurement of Salinometer S°/$_{oo}$	Error °/$_{oo}$
31.607	31.565	0.042
32.255	32.220	0.035
27.145	27.102	0.043
31.137	31.103	0.034

As may be seen from the table between sonde and salinometer there is a systematic error on the average +0.038°/$_{oo}$. It is used for the correction of the sonde.

As well as the static calibration a dynamic calibration of CTD sondes is necessary because of differences in the time constants of temperature and electroconductivity sensors when simultaneously measuring the parameters. Inductive sensors for electroconductivity are practically instantaneous and because of this the basic errors are found in the gauges of temperature. This error can be expressed by the equation as follows:

$$T_{DEN} = V \cdot \Theta \cdot \frac{dT}{dH} \qquad [47]$$

where T_{DEN} - dynamic error of measuring temperature at °C. arising out of the inertia of the gauge.

V - the speed of movement of sonde (m/s).

dT/dH - gradient of temperature by depth (degrees/m).

Θ - the actual inertia of the sonde (S), depending on the design and temperature parameters of the gauge, the condition of flow around it, the mass of the housing instrument, etc.

The error of the measurement of temperature introduces an error in definition of salinity:

$$\Delta S = \gamma_{TS} \cdot \Delta T_{DEN} \qquad [48]$$

where γ_{TS} - a coefficient equal to the error in calculation of salinity, corresponding to error of temperature measurement of 1°C.

Substituting equation [47] in [48] gives the formula for the dynamic error of salinity:

$$\Delta S = \gamma_{TS} \cdot V \cdot \Theta \cdot \frac{dT}{dH} \qquad [49]$$

With the usual decrease of temperature with depth the temperature inertia of CTD sondes in movement downwards causes a lowering of salinity values and movement upwards the opposite. On the graphs of the vertical sounding of temperatures and salinities, this is expressed as a hysteresis in lowering and raising the instrument (Figure 10).

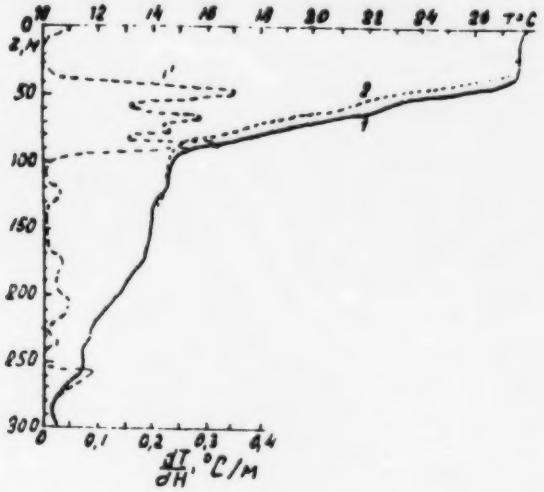


Figure 10: Hysteresis in profiles for temperature (curves 1 and 2) and "spikes" in salinity for calculating differences in the inertia in gauges T and S of electroconductivity by (18).

It is essential to take dynamic error into account. Equation [49] defined parameters. Even if the speed of movement of the probe is known, defining magnitudes of other parameters is difficult, especially if the actual time constant of the probe turns out to be significantly greater than rated values.

K.H. Fedorov and V.I. Prokhorov (18) proposed an original method of defining the sonde constant and calculating the dynamic error in measurement of salinity. Later Dantzler (45) used an analogous method: CTD sonde as a linear filter of real time. He found a theoretical solution of calculating dynamic error of measurement of salinity.

The method of determining the dynamic error and real time constant by (18) uses data derived from the sonde in the form of TS diagrams, accepting the effect of internal waves and changes of both parameters with depth (Figure 11).

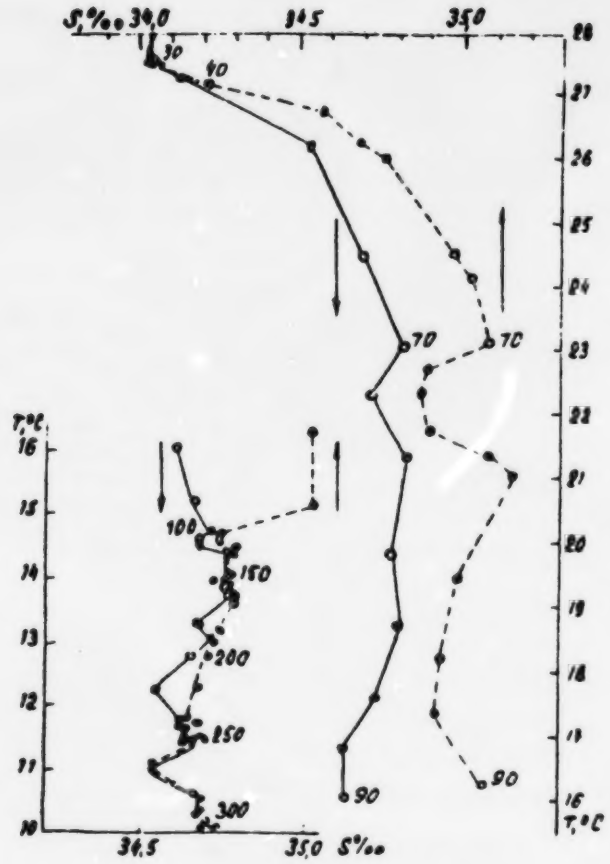


Figure 11: TS diagram for data of sonde at time of lowering and raising by (19).

On the ST diagram values of ΔS are found as half of the difference between the two profiles on a T - constant line. Taking ΔS values thus found and corresponding values of dT/dH a fit is made of S = f(dT/dH), having a normal probability distribution due to instrumental errors. Holding γ_{TS}, Θ and V constant in equation [49], the average of the (ΔS, dT/dH) points has a linear dependency

$$\Delta S = \alpha \frac{\partial T}{\partial H} \qquad [50]$$

Values of alpha from Figure 12 equal the product γ_{TS}, V, Θ. Coefficient γ_{TS} from (18), equals 0.86°/$_{oo}$ per °C, by data from (53) and (45) equals 0.92°/$_{oo}$ per °C and 0.96°/$_{oo}$ per °C respectively.

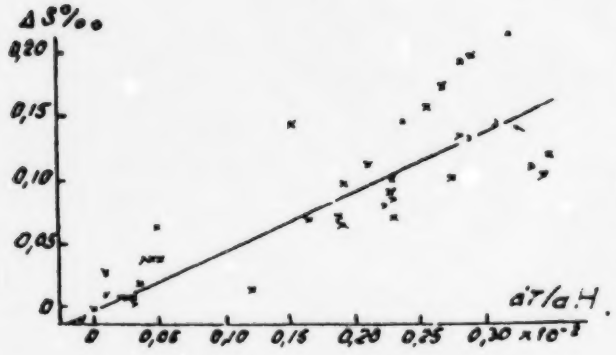


Figure 12: The linear relationship between dynamic error of salinity and temperature gradient.

The value of sonde's inertia is derived from:

$$\Theta = \frac{\alpha}{\gamma_{TS} \cdot V} \qquad [51]$$

In this way the dynamic calibration of sonde results in definitions of its actual time constant and allows correction of dynamic errors in salinity from measured data. The correction consists of spacing in time the interrogation of gauges of temperature and electroconductivity. An example of making use of such corrections is the sonde "ISTOK-3" in which measurement of temperature is made earlier than measurement of electroconductivity by 0.3 and 0.4 sec.

As a result of TS diagram points corresponding to parameters measured at lowering and raising of the sonde in practice lie on one line.

Discussing such a method of calibration, Dantzler (45) notes that for this method some limitations exist: the method gives unsatisfactory results in cases where irregularities have a vertical scale less than several metres.

CONCLUSIONS

Analysis of the materials available allow us to determine a set of goals which may be the subject of research. Essentially:

1. To test the influence of a concentration change of one or more saline components on electrical conductivity of sea water and the possibility of introducing corrections into the formula connecting salinity, electrical conductivity, temperature and pressure with the goal of calculating the influence of such changes.

2. To test the influence of physical-chemical alterations of sea water, taken from various depths by means of bottle samples on the differences in salinity measurements (from bottle samples) and from CTD sondes.

3. To exactly measure the specific electrical conductivity of normal water at 15°C with the goal of calibrating salinometers and CTD probe by specific electrical conductivity.

4. To carry out a comparison and an intercalibration of salinity measurement in laboratory conditions and in situ bringing to bear as many instruments as possible.

5. By experiment to determine the exact dependence of electrical conductivity on temperature from -2°C to 14°C.

6. For regions with anomalous waters or with waters that have significant fluctuations of ionic constituents to find regional dependencies of salinity and electrical conductivity, and to clarify the possibility of defining the dependency between electrical conductivity, temperature and pressure for each region.

7. To the regions of the world oceans, which have fairly constant relative ionic composition within errors not exceeding state-of-the-art measurement, to work out general formulae for transforming in situ measured values to salinity.

8. To check the applicability of the formula of Bradshaw and Schleicher outside the limits of the salinity range of data from which the formula was derived.

In conclusion it should be noted that many of our recommendations for further research agree with the recommendations of the UNESCO 6th Report of the Joint Panel on Oceanographic Tables and Standards.

REFERENCES

1. Alekin, O.A. On the significance of ionic runoff in oceans. Oceanology, 1967, 7, 4.

2. Almazov, A.M. On the methods of calculation of the salinity of open waters and estuaries and the concentration of their major ions. Hydrochemical Materials, 1957, 31.

3. Blinov, L.K. The saline content of sea water and ice. G.O.I.N. 1965, 83.

4. Bruevich, S.N. On the major saline content of ocean waters and calculation of salinity by Knudsen. I.O.A.N. 1961, 47.

5. Yerofeyev, P.N., E.P. Kalmykova, L.S. Ponomareva, E.B. Chernyavskii, Automated sounding hydraulic complexes and samplers for instruments. Summary Report, Series 9, Professional Oceanology, Release 1, M., Ch. I.I.T.E.I.R.K., 1973.

6. Zaburdaev, V.I., L.M. Dobruskina, E.F. Lyashenko, and M.G. Poplavskaya, 1969. A method of determination of salinity from specific conductivity,temperature and pressure of sea water. Oceanic Hydrological Investigation Report, No. 1 (43), Academy of Sciences, Ukrainian S.S.R., Sevastopol, 1969. pp 5.

7. Zubov, N.N. Oceanological Tables. Hydrometric Publication, L., 1957.

8. Ivanov-Frantskevitch, G.N. Panel of the U.N. Group to report on salinity standards. (Paris 23-25 May, 1962). Oceanology 1963, Vol. 3, No. 6.

9. International Oceanographic Tables, 1st ed., Hydrometric Publications, M., 1969.

10. Ponomareva, L.S. Physical and physio-chemical methods of defining the salinity of sea water. Summary Report, Series 1, Professional Ichthyology and Oceanology, Release 3, M., Ch. I.I.T.E.I.R.K., 1970.

11. Ponomareva, L.S. Study of the hydrochemical characteristics of the Baltic Sea. Review Information, Series 9, Professional Oceanology, Release 1, M., Ch. I.I.T.E.I.R.K., 1972.

12. Ponsov, A.G. Electroconductivity as a characteristic of the physio-chemical contents of sea and river water and a method of defining their salinities. G.O.I.N. 1960, Release 49.

13. Prokhorov, V.I., K.N. Fedorov, A.G. Volochkov. Attempt to calibrate at sea. Oceanology, 1973, Vol. 13, No. 3.

14. Selifonova, E.P., A.P. Tsurikova, M.P. Nesterova. Research on some physio-chemical characteristics of Soviet Normal Water. Chemistry of Seas and Oceans, Science, M., 1973.

15. Sopach, E.D. Electroconductivity as a method of defining the salinity of sea water. Hydrometric Publications, M., 1958.

16. Ungerman, M.N., P.K. Guber. The technology of oceanological observation on research and industrial ships. Food Industry, M., 1973.

17. Fedorov, K.N. Formulas for converting the electrical conductivity of sea water into salinity with a digital temperature-salinity probe under average ocean conditions. Oceanology, 11, 4, 1971.

18. Fedorov, N.K., V.I. Prokhorov. True response lag in temperature measurement and the reliability of ocean salinities determined with temperature-salinity probes. Atmospheric and Oceanic Physics. Vol. 8, No. 9, 1972, pp 998-1003.

19. Horne R. Chemistry of the sea. World, M., 1972.

20. Tsurikov, V.L. Formulation and changes of the salinity of sea ice. Chemical Resources of the seas and oceans, M., 1970.

21. Tsurikova, A.P. On the dependency between salinity, chlorinity and density of the waters of Azov Sea. G.O.I.N., 1960, Release 52.

22. Tsurikova, A.P., V.L. Tsurikov. Ion content of under ice waters. Oceanology, 1970, Vol. 10, No. 4.

23. Tsurikova, A.P., V.L. Tsurikov. The question of salinity. Oceanology, 1971, Vol. 11, No. 2.

24. Chernovskaya, E.N., N.M. Pastukhova, A.G. Buynevich, E.A. Ayuninsh, M.E. Kudryavtseva. Hydrochemical regime of the Baltic Sea. Hydrometric Publications, 1965.

25. Accerboni E., Mosetti F. A physical relationship among salinity, temperature and electrical conductivity of sea water. "Boll. di geofis. teor. ed appl.", 1967, 9, N. 34.

26. Adams, L.H., Hall R.E. The effects of pressure on the electrical conductivity of solutions of sodium chloride and of other electrolytes. "J. Phys. Chem.", 1931, 35, N 2145.

27. Bein, N., Hirskeborn H.G., Möller L. Konstantenbestimmungen des Meereswasser und Ergebnisse über Wasserkörper. "Veröff. Inst. für Meereskunde Berlin Univ.", 1935, 28 (239).

28. Bradshaw, A., Schleicher K.E. The effect of pressure on the electrical conductance of sea water. "Deep-Sea Res.", 1965, 12, N 2.

29. Broecker, W.S., Takahashi T. Calcium carbonate precipitation in the Bahama Banks. "J. Geophys. Res.", 1966, 71, N 6.

30. Brown, N.L., Allentoft B. Salinity, conductivity and temperature relationships of sea water and over the range 0-50°/$_{oo}$. Final report, March 1. Prepared for United States office of Naval Research. Contract N 4290(00), M.I.O. 1966, N 2003.

31. Carrit, D., Carpenter J. The composition of sea water and the salinity-chlorinity-density problems. "Publ. Nat. Acad. Sci. - Nat. Res. Council", 1959, N 600.

32. Collins, C.A., Healey D.A. Use of continuous recording STP instrumentation at ocean station P (50°N,145°W). "J. Fish. Res. Board Canada", 1972, 29, 323-327.

33. Conners, D., Kester D. Effect of major ion variations in the marine environment on the specific gravity-conductivity-chlorinity-salinity relationships. "Mar. Chem.", 1974, 2, N 4.

34. Connors, D., Park K. The partial equivalent conductances of electrolytes in sea water: a revision. "Deep-Sea Res.", 1967, 14, N 4.

35. Connors, D., Weyl P. The partial equivalent conductances of salts in sea water and the density conductance relationship. "Limn. and Oceanogr.", 1968, 13, N 1.

36. Cox, R.A. The constancy of the ratio between conductivity and chlorinity of sea water. ICES-Tagung., Kopenhagen., Hydr. Comm., 1959, N 110.

37. The operation of sea water sealed in glass tubes as a standard of conductivity. "ICES-Tagung., Kopenhagen., Hydro. Comm., 1959, N 111.

38. Cox, R.A. The salinity problem. "Progress in oceanogr.", 1963, 1.

39. Cox, R.A. Culkin F., Greenhalgh R., Riley J.P. Chlorinity, conductivity and density of sea water. "Nature", 1962, 193, N 4815.

40. Cox, R.A., Culkin F., Riley J.P. New investigations on the determination of salinity. "Cons. expl. mer. Hydr. Comm.", 1961, N 155.

41. Cox, R.A., Culkin F., Riley J.P. The electrical conductivity/chlorinity relationships in natural sea water. "Deep-Sea Res.", 1967, 14, N 2.

42. Cox, R.A., McCartney M.J., Culkin F. Pure water for relative density standard. "Deep-Sea Res.", 1968, 15, N 3.

43. Culkin F. The major constituents of sea water. "Chem. Oceanogr. V.I.". Acad. Press. London - New York, 1965.

44. Culkin F., Cox R.A. Sodium, potassium, magnesium, calcium and strontium in sea water. "Deep-Sea Res.", 1966, 13, N 5.

45. Dantzler, H.L. Dynamic salinity calibrations of continuous salinity/ temperature/depth data. "Deep-Sea Res.", 1974, 21, N 8.

46. Dittmar, W. Report on researches into the composition of ocean water, collected of the voyage "Challenger". "Phys. and Chem.", 1884, 1.

47. Fofonoff, N.P. Physical properties of sea water. "Sea", 1962, 1.

48. Forch, C., Knudsen M., Sørensen S. Berichte uber Konstantenbestimmungen zur Aufstellung der hydrographischen Tabellen. "D. Kgl. Danske Vidensk. Selsk. Skrifter". Raekke, Naturvidensk. og Mathem. Afg XII, 1902.

49. Garrels, R.M., Thomson M.E. A chemical model of sea water at 25°C and one atmosphere total pressure. "Amer. J. Sci.", 1962, 260, N 1.

50. Gibbs, R.J. Mechanisms controlling world water chemistry. "Science", 1970, 170, N 3962.

51. Gopinathan C.K., Qasim S.Z. A critique on chlorinity, salinity and electrical conductivity interrelationship of sea water. "J. Mar. Biol. Ass. India", 1972, 14, N 1.

52. Greenhalgh, R., Riley J.P. Occurance of abnormally high fluoride concentrations at depth in the oceans. "Nature", 1963, 197 (371-372).

53. Gregg, M.C., Cox C.S. Measurements of the oceanic microstructure of temperature and electrical conductivity. "Deep-Sea Res.", 1971, 18, N 9.

54. Grindley, J. The determination of the salinity of water in estuaries. "Assoc. intern. sci.", 1960, 51.

55. Groh, G. Über den Druckeinfluß auf das electricshe Leitvermöden von Meerwasser. "Zeitcshrift für angewandte Physik", BDV, 1963, 42.

56. Hamon, B.V. The effect of pressure on the electrical conductivity of sea water. "J. Marine Res.", 1958, 16, N 1.

57. Horne, R.A. The physical chemistry and structure of sea water. "Water resources res.", 1965, N 1.

58. Horne, R.A., Courant R.A. Application of Walden's rule to the electrical conduction of sea water. "J. Geophys. Res.", 1964, 69, N 10.

59. Horne, R.A., Frysinger G.R. The effect of pressure on the electrical conductivity of sea water. "J. Geophys. Res.", 1963, 68, N 7.

60. Jacobsen, J.R., Knudsen M. Urnormal 1937 or primary standard sea water. "Assoc. Oceanogr. Physique Publ. Scient.", 1940, N 1.

61. Jaeger, J.E. The determination of salinity from conductivity temperature and pressure measurements. "Proc. second S/T/D conf. and workshop", San Diego, Calif. USA, 1973.

62. Jonston, R. Recent advances in the estimation of salinity. "Oceanogr. and mar. biol. Ann. Rev.", 1964, 2.

63. Jonston, E. On salinity and its estimation. "Oceanogr. and mar. biol. Ann. Rev.", 1969, 7.

64. Kato, K. Studies on calcium content in sea water. II.Distribution of calcium in the Atlantic water off South Brazil. "Bol. Inst. oceanogr.", 1966, 15, N 1.

65. Kester, D., Pytkowicz, M. Sodium, magnesium and calcium sulfate ion-pairs in sea water at 25°C. "Limnol. and Oceanogr.", 1969, 14, N 5.

66. Kester, D., Pytkowicz, M. Effect of temperature on sulfate ion association in sea water. "Geochim. at cosmochim. acta", 1970, 34, N 10.

67. Kirch, M. Ionic ratios of some of the major components in river diluted sea water in Bute and Knight Inlets, British Columbia. "J. Fish. Res. Board Canada", 1956, 13, 3.

68. Klotz, J.M. Comment on the variation of solubility with depth. "Limnol. and Oceanogr.", 1963, 8, N 4.

69. Knowles, C.E. Salinity determination from the use of STD sensors. "J. Phys. Oceanogr.", 1974, 4, N 2.

70. Knudsen, M. Hydrographishe Tabellen, Copenhagen, 1901.

71. Koszy, F.F. The specific alkalinity. "Deep-Sea Res.", 1956, 3, N 2.

72. Kremling, K. Relation between chlorinity and conductometric salinity in Black Sea water. "Black Sea - Geol., chem. and biol.", Tulsa, Okla. 1974.

73. Krümmel, O. Handbuch der Oceanographie. Stuttgart, 1907.

74. Kwiecinski, B. The relation between chlorinity and the conductivity in Baltic water. "Deep-Sea Res.", 1965, 12, N 2.

75. Lewis, E.,Sudar R. Measurement of conductivity and temperature in the sea for salinity determination. "J. Geophys. Res.", 1972, 77, N 33.

76. Lyman, J. Chemical considerations. "Publ. Nat. Acad. Sci. - Nat. Res. Council", 1959, N 600.

77. Lyman, J., Fleming R.N. Comparison of sea water. "J. Marine Res.", 1940, N 3.

78. Magazzu, G. Il problema della salinita nelle acque salmastre. "Atti. Soc. pelorit. sci. fis., mat. e natur", 1966, 12, N 3-4.

79. Mameli, D., Mosetti, F. Un nuovo metodo di marcatura delle acque di mare costiere. "Boll. geofis. teor e appl.", 1966, 8, N 32.

80. Miyake, Y., Sugiura Y., Park, K. Effect of CO_2 - syster components on the electrical conductivity of deep-sea water. "The fourth deep-sea symposium". Tokyo, 1964, 2.

81. Monaco, A. Sur quelques phénimènes d'échanges ioniques dans les suspensions argileuses an contact de l'eau de mer.", C.R. Acad. sci.", 1970, D270, N 14.

82. Morcos, S., Riley, J.P. Chlorinity, salinity, density and conductivity of sea water from the Suez Canal region. "Deep-Sea Res.", 1966, 13, N 4.

83. Morris, A.W., Riley, J.P. The direct gravimetric determination of the salt in sea water. "Deep-Sea Res.", 1964, 11, N 6.

84. Morris, A.W., Riley, J.P. The bromide/chlorinity and sulphate/chlorinity ratio in sea water. "Deep-Sea Res.", 1966, 13, N 4.

85. Mosetti, F. Una nuova formula per la conduttivita dell'acqua di mare in funzione della temperatura e della salinita. "Boll. geofis. teor e appl.", 1966, 8, N 13.

86. Nehring, D., Rohde K. H. Anomale Ionenverhältnisse in der Ostsee. "Monatsber. Dtsch. Acad. Wiss. Berlin", 1966, 8, N 5.

87. Park, K. Electrolytic conductance of sea water: effect of calcium carbonate dissolution. "Science", 1964, 146, N 3640.

88. Park, K. Partial equivalent conductance of electrolytes in sea water. "Deep-Sea Res.", 1964, 11, N 5.

89. Park, K. Reliability of standard sea water as conductivity standard. "Deep-Sea Res.", 1964, 11, N 1.

90. Park, K. Columbia River plume identification by specific alkalinity. "Limnol. and Oceanogr.", 1966, 11, N 2.

91. Park, K., Bradshaw, A., Menzel, D., Schleicher, K., Curl, H. Changes in electrolytic conductance of sea water during photosynthesis and respiration. "J. Ocean. Soc. Japan", 1969, 25, N 3.

92. Park, K., Burt V. Experimental determination of reliability of an inductive salinometer. Presented at Amer. Soc. Limnol. and Ocean. Pacific Div., Stanford, Calif., June 1963.

93. Park, K. Electrolytic conductance of sea water and the salinometer. "J. Ocean. Soc. Japan", 1965, 21, N 2-3.

94. Park, K. Effect of photosynthesis and respiration on the electrical conductance of sea water. "Nature", 1965, 205, N 4968.

95. Park, K., Weyl, P., Bradshaw, A. Effect of carbon dioxide on the electrical conductance of sea water. "Nature", 1964, 201, N 4926.

96. Perkin R., Walker, E. Salinity calculations from in situ measurements. "J. Geophys. Res.", 1972, 77, N 33.

97. Platford, R.F. The activity coefficient of sodium chloride in sea water. "J. Marine Res.", 1965, 23, N 2.

98. Platford, R.F. Activity coefficient of sodium ion in sea water. "J. Fish. Res. Board Canada", 1965, 22, N 4.

99. Platford, R.F. Dafoe, T. The activity coefficient of sodium sulfate in sea water. "J. Marine Res.", 1965, 23, N 2.

100. Pollak, M.G. The use of electrical conductivity measurement for chlorinity determination. "J. Marine Res.", 1954, 13, N 2.

101. Postma, H. The exchange of oxygen and carbon dioxide between the ocean and atmosphere. "Neth. J. Sea Res.", 1964, 2, (252).

102. Pytkowicz, R.M. Gravity and the properties of sea water. "Limnol. and Oceanogr.", 1963, 8, N 2.

103. Reeburgh, W.S. Measurements of the electrical conductivity of sea water. "J. Marine Res.", 1965, 23, N 3.

104. Riley, J.P. The occurance of anomalously high fluoride concentrations in the north Atlantic. "Deep-Sea Res.", 1965, 12, N 2.

105. Riley, J.P. Tongudai, M. The major cation/chlorinity ratios in sea water. "Chem. Geol.", 1967, 2, N 3.

106. Ruppin, E. Bestimmung der elektricshen Leitfähigkeit. "Wiss. Meeresuntersuch.", Kiel, IX, H 4, 1906.

107. Sagi, T. The concentration of calcium/chlorinity ratio in the western North Pacific Ocean "Oceanogr. Mag.", 1969, 21, N 1.

108. Sankey, B.A. Some problem in the asgusition data with a STD probe. "Proc. IEEE Conf.", 1968, N 8.

109. Shanklin, D.R. Cation analysis of Woods Hole sea water. "Nature", 1954, 173, N 4393.

110. Smith, C.L. The Great Bahama Bank. Calcium carbonate precipitation. "J. Marine Res.", 1940, III, N 2.

111. Sugiura, Y. The significance of the difference in conductometric chlorinity minus titrimetric chlorinity. "Rec. Oceanogr. Works, Japan", 1967, 9, N 1.

112. Tackabery, R.E. Deep ocean STD measurements. "Oceanol. Intern.", 1969, Sept/Oct.

113. Thomas, B., Thomson, T. Utterback, C. Refractivity-chlorinity-temperature relationships of ocean waters. "J. Cons. Perm. Int. Explor. Mer.", 1934, 9. (28-35).

114. Tsunogai, S., Nishimura, M., Nakaya, S. Calcium and magnesium in sea water and the ratio of calcium to chlorinity as a tracer of water masses. "J. Ocean. Soc. Japan", 1968, 24, N 4.

115. UNESCO. Reports of joint panel on the equation of state of sea water, 1962, Paris, 4. NS/9/114B.

116. UNESCO. 1st report of the joint panel on oceanographic tables and standards. "Unesco techn. papers in marine sci. N 1", 1964.

117. UNESCO. 2nd report of joint panel on the equation of state of sea water. Bercley, Calif., 19, NS/9/114B and in "UNESCO techn. papers in mar. sci", 1966.

118. UNESCO techn. papers in Marine Sci. N 8 3rd report on the joint panel on oceanographic tables and standards, 1967.

119. UNESCO. 6th report of the joint panel on oceanographic tables and standards. "UNESCO techn. papers in mar. sci.", N 16, 1973.

120. Walker, E.R. A comparison of salinity equations. "Proc. second STD conf. and workshop", San Diego, Calif. USA, 1973.

121. Walker, E.R. Chapman, E.R. Salinity-conductivity formulae compared. Pacific mar. sci. rep. 73-5", 1973.

122. Wallace, W. The development of the chlorinity/salinity concept in oceanography. (Elsevier Oceanogr. Ser., 7) Amsterdam e.e., Elsevier Sci. Publ. Col, 1974, XII.

123. Weyl, P.K. On the change of electrical conductance of sea water with temperature. "Limnol. and Oceanogr.", 1964, 9, N 1.

124. Wooster, W.S., Lee, A.G. Dietrich, G. Redefinition of salinity. "Limnol. and Oceanogr.", 1969, 14, N 3.